Water Molecule Dipole in the Gas and in the Liquid Phase

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We study with *ab initio* molecular dynamics the change that the electric dipole moment of water molecules undergoes in passing from the gas to the liquid phase. Our analysis is based on the recently introduced maximally localized Wannier functions and is devoid of the ambiguities that have affected previous attempts. We find that in the liquid the dipole moment has an average value of about 3 D, 60% higher than in the gas phase. This value is much larger than is currently assumed (2.6 D). Furthermore, a broad distribution around this average value is observed. The relevance of these results for current modeling of water is discussed. [S0031-9007(99)08956-5]

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The value of the water molecule dipole moment μ in liquid water plays a crucial role in determining the dielectric properties of this most important polar solvent and has clear repercussions on its physical, chemical, and biological behavior. In the gas phase it is well established experimentally [1] that $\mu = 1.86$ D. Theoretical calculations [2,3] of various levels of sophistication are in good agreement with this result. In the condensed phases the self-consistent internal electric field polarizes the water molecules, leading to a large increase of μ. The only firm evidence of this phenomenon comes from the remarkable study [3] of Gregory *et al.* about the dipole moment of clusters of up to 6 water molecules. By combining the results of experiments based on far-IR vibration-rotation-tunneling spectroscopy and very accurate *ab initio* calculations it has been shown that μ increases, as a function of the system size, up to a value of 2.7 D for the largest cluster. In liquid water this increase has not been determined experimentally and the most quoted values are obtained by performing semiempirical calculations on models of ice. The most commonly accepted value is 2.6 D, obtained by Coulson and Eisenberg [4] on ice I_h and this value is normally assumed to be appropriate for liquid water as well. However, this estimate has been challenged by various authors, and most recently the analysis of Coulson and Eisenberg has been repeated [5] using more modern input information, leading to $\mu = 3.09$ D. Moreover, other theoretical studies [6] on ice lattices have suggested that μ could be of the order of (or even larger than) 3.0 D. The dispute is far from being academic. On the one hand, it is important to understand how water molecules are modified when brought into the liquid environment. On the other, most potentials used in computer modeling of water try to reproduce the 2.6 D value and it is believed [7] that larger values would lead to incorrect modeling of the dielectric properties. The change in the dipole moment, in going from the gas to the condensed phase, cannot be reproduced by empirical models unless they explicitly take electronic polarization into account. To overcome this deficiency some models [8], based on the so-called "polarizable potentials," try to mimic the polarization effects of the liquid phase by including the dipole moment induced in a single water molecule, due to the presence of the surrounding molecules. However, these procedures are still approximate and simulations using different polarizable potentials lead to rather different estimates of μ (in the range 2.5–3.1 D). It is therefore difficult to assess the reliability of these methods.

In the lack of experiments, it is important to compute the value of μ in liquid water in a more satisfactory way. *Ab initio* molecular dynamics calculations offer in principle such a possibility. To this end we have performed a large-scale *ab initio* simulation. The only previous *ab initio* estimate [9] was $\mu \sim 2.7$ D. However, in the simulation of Ref. [9] a smaller system and a smaller basis set were used than in the present one; moreover, there was considerable uncertainty in the precise value of μ. This was determined by integrating the charge distribution around the water molecules up to a spherical cutoff. The value of μ was therefore dependent on the choice of cutoff.

Here, using a much more rigorous approach for the evaluation of μ, and a well-converged calculation, we find that the average dipole moment of a water molecule in the liquid is $\mu \sim 3.0$ D, with large fluctuations around this value. Crucial to our analysis is the use of the maximally localized Wannier function formalism [10]. This allows the total charge to be partitioned, in a chemically transparent and unambiguous way, into individual molecular contributions and provides an extremely useful tool to analyze the modification induced in the water molecules by the condensed phase. The maximally localized Wannier functions are a generalization to infinite periodic systems of the Boys localized orbitals [11] $w_n(\mathbf{r})$. These are obtained by performing a unitary transformation in the subspace of the occupied molecular orbitals (MO) so as to minimize the spread,

$$S = \sum_n (\langle r^2 \rangle_n - \langle \mathbf{r} \rangle_n^2)\,. \tag{1}$$

In Eq. (1) $\langle \ldots \rangle_n$ indicates the expectation value with respect to the nth orbital $w_n(\mathbf{r})$. The Boys orbitals bring out the chemistry of the system rather more clearly than the MOs. For instance, in water the valence electrons can be localized in two covalent orbitals that lie along the OH bonds, and two lone pair orbitals. For the analysis of a large system, however, it is essential to contract the information contained in the Wannier functions to a manageable level. To this end, if periodic boundary conditions are used with a cubic supercell of side L, we define [10] the coordinate x_n of the nth Wannier-function center (WFC) as

$$x_n = -\frac{L}{2\pi}\,\mathrm{Im}\,\ln\langle w_n|e^{-i(2\pi/L)x}|w_n\rangle, \tag{2}$$

with similar definitions for y_n and z_n.

The dipole moment μ of a water molecule can be calculated from the total charge density or equivalently, as discussed in Refs. [10,12], from the ion and WFC positions, by assuming that the electronic charge is concentrated in point charges located on the WFCs. We have calculated the WFCs for an isolated water molecule by optimizing the structure in a cubic supercell of side $L = 10.6$ Å. The computations [13] have been performed at the Γ point only of the Brillouin zone, using norm-conserving pseudopotentials [14] with a plane-wave cutoff of 70 Ry and a gradient-corrected Becke-Lee-Yang-Parr (BLYP) [15] density functional. Since we use the pseudopotential approximation, we explicitly consider 8 electrons per water molecule, the 2 additional oxygen-core electrons being essentially inert from the point of view of the bonding properties. Because of spin degeneracy we need therefore to consider 4 doubly occupied Wannier functions and their relative WFCs.

In the case of the isolated water molecule the WFCs are tetrahedrally oriented and their distance from the oxygen atom is 0.53 and 0.30 Å for covalent bond and lone pair orbitals, respectively (see Fig. 1). Using these data we compute a molecular dipole moment of 1.87 D, in excellent agreement with the experimental value [1] (1.86 D). We then apply the same procedure to analyze the dipole moments of water clusters. We calculate the Wannier functions and, using the WFCs, we evaluate the dipole moments of each water molecule. We find that the average value of μ is 2.1 D in the water dimer and 2.4 D in the water trimer. These values are in good agreement with those reported in Ref. [3] (2.1 and 2.3 D, respectively). This gives us confidence in the usefulness of the localized orbital analysis of the dipolar structure of coordinated water. We then extend the analysis to bulk water. To this effect we performed a simulation on 64 water molecules, using truncated octahedral periodic boundary conditions, at $\rho = 1$ g/cm^3 density and an average ionic temperature of 318 K. The other details of the calculations were as in the isolated molecule calculation [the generalization of Eq. (2) to nonsimple cubic supercells will be reported elsewhere [16]]. The Car-Parrinello equations [17] were integrated using a fictitious electronic mass parameter of 900 a.u. and a molecular dynamics time step of 0.145 fs. After an equilibration time of 2 ps averages were collected for about 10 ps.

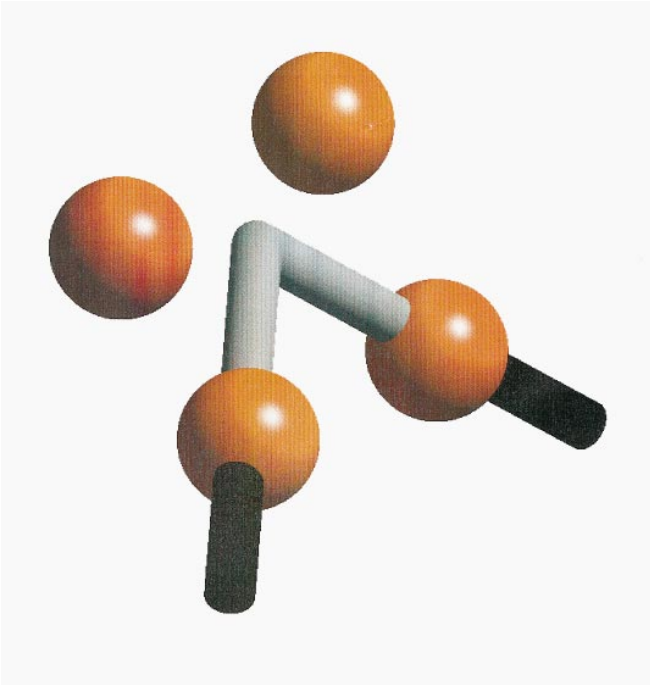

FIG. 1(color). Water molecule in the gas phase. The sticks represent the OH bonds while the red balls indicate the positions of the WFCs.

We show in Fig. 2 the resulting oxygen-oxygen pair correlation function $g_{\mathrm{OO}}(r)$ and compare it to the most recent neutron scattering data [18] as well as to the older

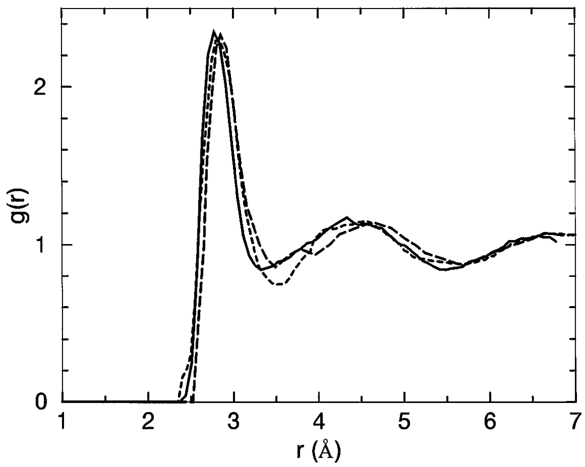

FIG. 2. OO pair correlation function obtained from our *ab initio* simulation (solid line), compared to the experimental neutron scattering [18] (dashed line) and x-ray diffraction [19] (long-dashed line) curves.

x-ray estimate [19]. Note that, in the earlier neutron scattering analysis [20], the first $g_{\mathrm{OO}}(r)$ peak turned out to be substantially higher and that most empirical water potentials have been fitted to this higher value. As can be seen both the positions and the intensities of the first three maxima are very close to the experimental values. Also the less controversial $g_{\mathrm{OH}}(r)$ and $g_{\mathrm{HH}}(r)$ pair correlation functions are in good agreement with the experimental curves. We have also evaluated the diffusion coefficient, which is $D = 2.8 \pm 0.5 \times 10^{-5}$ cm^2/sec, in good agreement with the experimental value [21] $D = 2.4 \times 10^{-5}$ cm^2/sec. Having established that our level of theory is satisfactory in comparison with experiments we turn to the analysis of the dipole moment. For us a water molecule in bulk water is composed of the H_2O ionic cores and its 4 Wannier orbitals. The validity of this partition can be judged by the amount of overlap between the charge distribution of Wannier functions associated with different molecules. This turns out to be rather small. In fact, the spread of the Wannier functions is found to be $(\langle r^2\rangle_n \langle \mathbf{r}\rangle_n^2)^{1/2} \sim 0.7$ Å, much smaller than the intermolecular distances; moreover, we measure the charge overlap O_{mn} between two Wannier functions as

$$O_{mn} = \frac{\int d\mathbf{r}\, |w_m(\mathbf{r})|^2 |w_n(\mathbf{r})|^2}{(\int d\mathbf{r}\, |w_m(\mathbf{r})|^2 |w_m(\mathbf{r})|^2)^{1/2} (\int d\mathbf{r}\, |w_n(\mathbf{r})|^2 |w_n(\mathbf{r})|^2)^{1/2}}, \tag{3}$$

and we find that O_{mn} is about 0.2 for different Wannier functions of the same water molecule, while it is smaller than 0.01 for Wannier functions located on different molecules.

The distribution of the intramolecular O-WFC distances in the liquid can be analyzed by looking at the O-WFC pair correlation function. This is shown in Fig. 3, where it can be seen that, with respect to the case of the isolated molecule, in the bulk the lone pair orbitals are pulled out due to the formation of the hydrogen bonds, while the covalent bond orbitals are pulled in (the average O-WFC distances are 0.33 and 0.50 Å, respectively). This indicates that, in the condensed phase, the electronic charge is more spherically distributed around the oxygen atoms than in the gas phase. Since, in addition, our structural analysis shows that in the liquid phase the average OH intramolecular bond length is about 2% larger than in the isolated molecule, this behavior can also be viewed as a charge-transfer process in which, upon hydrogen bonding, the hydrogen atoms lose electrons in favor of the oxygens. As a consequence of the polarization effects of the surrounding molecules, the values of the molecular dipole moments are characterized (see Fig. 4) by a broad distribution whose average value is 2.95 D, considerably larger than the current estimate. Note that the probability distribution is not symmetric and that some water molecules have a dipole moment as large as 4 D. In rigid ion models for water it is assumed that all water molecules are equal. This is clearly contradicted by the very broad distribution of Fig. 4.

We are aware of the limitations of the present simulation in terms of both size and time scale. However, it seems to us that it is time to revisit critically the current water models. Most of them are obtained by fitting empirical data. Two important quantities play a major role in the fitting procedure: the $g_{\mathrm{OO}}(r)$ pair correlation function of the older neutron scattering analysis, which is rather more structured than more recent analysis and x-ray diffraction suggest, and the dipole moment which is taken to be $\mu \sim 2.6$ D. Either set of data could be inaccurate. In view of the relevance of water we would like to call

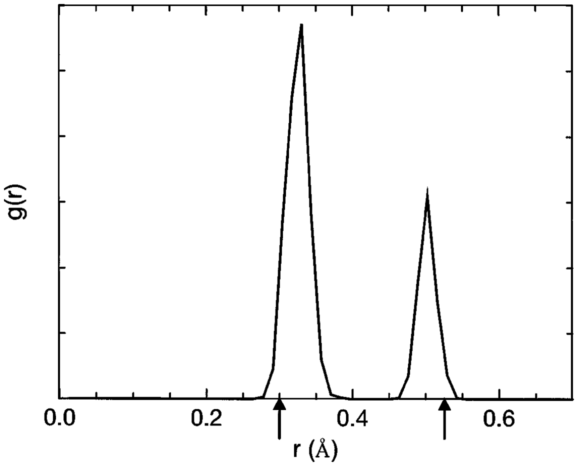

FIG. 3. O-WFC pair correlation function in liquid water. The arrows denote the O-WFC distances in the isolated water molecule. Data for the liquid phase were obtained by averaging over 12 configurations of the molecular dynamics simulation.

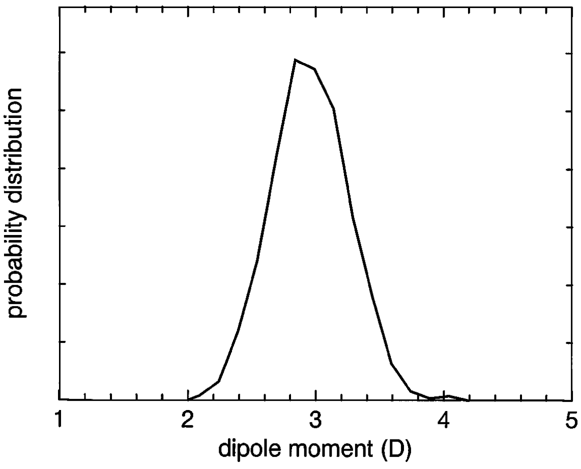

FIG. 4. Distribution of the modulus of the water molecule dipole moment in liquid water, by considering 12 molecular dynamics configurations.

on the experimental community to redouble its efforts to determine $g_{OO}(r)$ in a definitive way. It would also be extremely useful to have a direct experimental measure of μ in liquid water.

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[1] S. A. Clough, Y. Beers, G. P. Klein, and L. S. Rothman, J. Chem. Phys. **59**, 2254 (1973).

[2] S. S. Xantheas and T. H. Dunning, Jr., J. Chem. Phys. **99**, 8774 (1993).

[3] J. K. Gregory, D. C. Clary, K. Liu, M. G. Brown, and R. J. Saykally, Science **275**, 814 (1997).

[4] C. A. Coulson and D. Eisenberg, Proc. R. Soc. London A **291**, 445 (1966).

[5] E. R. Batista, S. S. Xantheas, and H. Jónsson, J. Chem. Phys. **109**, 4546 (1998).

[6] D. J. Adams, Nature (London) **293**, 447 (1981); M. I. Heggie, C. D. Latham, S. C. P. Maynard, and R. Jones, Chem. Phys. Lett. **249**, 485 (1996); E. Whalley, Chem. Phys. Lett. **53**, 449 (1978).

[7] S. L. Carnie and G. N. Patey, Mol. Phys. **47**, 1129 (1982); K. Watanabe and M. L. Klein, Chem. Phys. **131**, 157 (1989); M. Sprik, J. Chem. Phys. **95**, 6762 (1991).

[8] M. Sprik and M. L. Klein, J. Chem. Phys. **89**, 7556 (1988); U. Niesar, G. Corongiu, E. Clementi, G. R. Kneller, and D. K. Bhattacharya, J. Phys. Chem. **94**, 7949 (1990); J. P. Brodholt, M. Sampoli, and R. Vallauri, Mol. Phys. **86**, 149 (1995).

[9] K. Laasonen, M. Sprik, and M. Parrinello, J. Chem. Phys. **99**, 9080 (1993).

[10] N. Marzari and D. Vanderbilt, Phys. Rev. B **56**, 12847 (1997); P. L. Silvestrelli, N. Marzari, D. Vanderbilt, and M. Parrinello, Solid State Commun. **107**, 7 (1998).

[11] S. F. Boys, in *Quantum Theory of Atoms, Molecules, and the Solid State*, edited by P.-O. Löwdin (Academic Press, New York, 1966), p. 253.

[12] D. Vanderbilt and R. D. King-Smith, Phys. Rev. B **48**, 4442 (1993).

[13] We have used the code CPMD, version 3.0, developed by J. Hutter, P. Ballone, M. Bernasconi, P. Focher, E. Fois, S. Goedecker, M. Parrinello, and M. Tuckerman, at MPI für Festkörperforschung and IBM Zurich Research Laboratory (1990–1996).

[14] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[15] A. D. Becke, Phys. Rev. A **38**, 3098 (1988); C. Lee, W. Yang, and R. C. Parr, Phys. Rev. B **37**, 785 (1988); M. Sprik, J. Hutter, and M. Parrinello, J. Chem. Phys. **105**, 1142 (1996).

[16] P. L. Silvestrelli, Phys. Rev. B (to be published).

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

[18] A. K. Soper, F. Bruni, and M. A. Ricci, J. Chem. Phys. **106**, 247 (1997).

[19] A. H. Narten and H. A. Levy, J. Chem. Phys. **55**, 2263 (1971).

[20] A. K. Soper and M. G. Phillips, Chem. Phys. **107**, 47 (1986).

[21] K. Krynicki, C. D. Green, and D. W. Sawyer, Faraday Discuss. Chem. Soc. **66**, 199 (1978).