A fully polarizable and dissociable potential for water

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Abstract

A new classical interaction potential for water simulations is presented. Water is modeled as a fully dissociable set of atoms with a point dipole, determined self-consistently, on every oxygen atom. The oxygen polarizability is not fixed but depends on the geometry of the system. We show that, in spite of the limited number of free parameters, the model reproduces the geometrical and vibrational properties of microclusters in a satisfactory way.

Water, being arguably the most important liquid in our life, has always attracted a great deal of attention from physicists and chemists. It is also a rather difficult substance to model, and, in spite of vast improvements in numerical techniques, \textit{ab-initio} simulations are not yet able to simulate more than a hundred molecules for a reasonable time. Many classical potentials have been proposed, but very few of them are able to take into account all the important structural and dynamical features of water. Dissociability, for instance, is important in order to describe bulk water and its hydration and proton-transfer properties. Polarizability is crucial in the description of structural properties.

In this Letter we propose a new dissociable and polarizable potential for water and validate it by means of the study of the geometrical and vibrational properties of the water molecule and of the water dimer and trimer; results on larger clusters, and a full comparison with other potentials, will be presented in a full paper. The validation process we used is especially stringent as we predict a range of physical properties much larger than usually done in this kind of studies. We believe this gives a better guarantee of transferability to

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our potential than the usual procedures. Our potential contains a small number of parameters and is based on reasonable physical assumptions, which include some quantum effects previously neglected. Its aim is to reunite the advantages of dissociable and polarizable potentials while at the same time keeping a comparatively simple and physically transparent form.

We assume that, in the molecule, most of the electric charge of each hydrogen is transferred to the oxygen. We also assume that the electronic polarizability of the molecule is entirely due to the oxygen. Several models already exist that allow one to treat successfully ionic crystal structures (see for instance [1,2,3]), and we will start from there. The potential we propose has the following form:

\[
U = U_{ZZ} + U_{BM} + U_{DD} + U_{VW} + U_{ZD} + U_{SR}.
\]

In the term

\[
U_{ZZ} = \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j}{r_{ij}} \tag{1}
\]

\(Z_o\) and \(Z_h\) indicate ionic charges and are considered as adjustable parameter, bound by the charge neutrality constraint \(Z_o + 2Z_h = 0\) and \(r_{ij} = r_i - r_j\), where \(r_i\) is the position of the \(i\)-th nucleus. The Born-Mayer repulsive term

\[
U_{BM} = \frac{1}{2} \sum_{i \neq j} f(\rho_i + \rho_j) \exp \left( \frac{R_i + R_j - r_{ij}}{\rho_i + \rho_j} \right) \tag{2}
\]

includes the adjustable parameters \(f, R_o, R_h, \rho_o, \rho_h\). The term

\[
U_{DD} = \frac{1}{2} \sum_{i \in O} \sum_{j \in O, j \neq i} \left( \frac{p_i \cdot p_i}{r_{ij}^3} - \frac{3(p_i \cdot r_{ij})(p_j \cdot r_{ij})}{r_{ij}^5} \right) + \sum_{j \in O} \frac{p_j^2}{2\alpha_o} \tag{3}
\]

describes dipole-dipole interaction, \(p_i\) being a point dipole located on the \(i\)-th oxygen, and the bare oxygen polarizability \(\alpha_o\) is taken as a further parameter; since hydrogen is almost entirely deprived of electrons, it is considered unpolarizable. The Van der Waals term is written as

\[
U_{VW} = -\frac{1}{2} \sum_i \sum_{j \neq i} \frac{c_i c_j}{r_{ij}^6} \tag{4}
\]

while the term

\[
U_{ZD} = \sum_{j \in O} \sum_{i \neq j} p_j \cdot Z_j \frac{r_{ij}}{r_{ij}^3} \tag{5}
\]
describes the charge-dipole interaction. The term

\[
U_{SR} = - \sum_{i \in H} \sum_{j \in O} p_j \cdot B(r_{ij}) \frac{r_{ij}}{r_{ij}}, \quad B(r_{ij}) = \frac{F}{\alpha_o} \exp\left(\frac{R_{sr_i} + R_{sr_j} - r_{ij}}{\rho_i + \rho_j}\right)
\]  

(6)

is taken from Ref.[2], where the polarizability in the shell model is studied. Intuitively, this term reduces the polarizability of oxygen by taking into account the interaction between its electronic charge and that of the closest hydrogen atoms, so it is not surprising that it has the same form of Eq. 2. In principle the values considered for \( R_{sr_o} + R_{sr_h} \) (only the sum of these parameters is relevant) are independent of \( R_o + R_h \), but in practice they are only slightly different, and in some previous studies [2] they were set as equal.

In almost all this work we set \( \rho_h = 0 \), that is we neglected the short-range hydrogen-hydrogen interactions given by Eqs. 2 and 6. In short, our potential is characterized by 11 independent parameters, which are listed in Table 1 together with their optimized values.

\[
\begin{align*}
Z_h &= 0.80e \quad \rho_h = 0 \\
Z_o &= -2Z_h = -1.60e \quad \rho_o = 0.209\AA \\
f &= 0.03405e^2\AA^{-2} \quad \alpha_o = 1.027\AA^3 \\
R_h &= 0.012\AA \quad F = 0.29e^{-1}\AA^3 \\
R_o &= 1.718\AA \quad c_h = 0.01e\AA^{5/2} \\
R_{sr_h} + R_{sr_o} &= 1.77\AA \quad c_o = 3.9e\AA^{5/2}
\end{align*}
\]

Table 1
Optimized set of parameters

It is worth noting that the optimized value of \( \alpha_o \) lies approximately midway between the polarizabilities of oxygen and of the water molecule. We fitted several physical quantities we considered of primary interest: of the monomer, the geometrical data, the vibrational frequencies and the dipole moment, all of them known experimentally. Of the clusters, the geometrical data relative to the equilibrium configurations, which are known experimentally and sometimes from \textit{ab-initio} calculations. The equilibrium geometries were found using a simple steepest-descent algorithm, with \( p_i \) determined self-consistently, while the vibrational frequencies were obtained via numerical calculation and diagonalization of the dynamical matrix. After fixing the parameters of the potential, as a further test we calculated the cluster binding energies, the vibrational frequencies and some configurations considered as local minima of the potential energy as reported also in some \textit{ab-initio} studies, comparing all these data with those found in the literature.

In the rest of this paper we shall use the following symbols: \( \mu \) for the dipole moment of the molecule; \( \nu_{ss}, \nu_{as} \) and \( \nu_b \) for the molecule normal modes, that is, re-
spectively, symmetric stretching, asymmetric stretching and bending; $\mu$(molec) is the average molecular dipole moment in the clusters. The subscripts b and f indicate the bond and free hydrogens, respectively.

Table 2
Molecule data

|         | Exptl data       | ab-initio[14] | This work |
|---------|------------------|---------------|-----------|
| d(O-H)  | 0.957Å[4]        | 0.965Å        | 0.961Å    |
| $\theta_{H-O-H}$ | 104.5°[4]     | 103.8°        | 104.5°    |
| $\nu_b$ | 1595cm$^{-1}$[5] | 1623cm$^{-1}$ | 1158cm$^{-1}$ |
| $\nu_{ss}$ | 3657cm$^{-1}$[5] | 3807cm$^{-1}$ | 3609cm$^{-1}$ |
| $\nu_{as}$ | 3756cm$^{-1}$[5] | 3936cm$^{-1}$ | 3234cm$^{-1}$ |
| $\mu$   | 1.86D[6]         | 1.87D[9]      | 2.07D     |

Table 3
Dimer structural data

|         | Exptl*/ab-initio$^\dagger$ data | This work |
|---------|---------------------------------|-----------|
| d(O - O) | 2.98Å[7]$^*$                   | 3.20Å     |
| $\theta(O - H_b - O)$ | 174° ± 10°[7]$^*$ | 171°      |
| d(O - H)$_b$ | 0.972Å[14]$^\dagger$ | 0.98Å     |
| d(O - H)$_f$ | 0.964-0.966Å[14]$^\dagger$ | 0.960-0.968Å |
| $\theta_a$ | 57° ± 10°[8]$^*$              | 92°       |
| $\theta_d$ | 51° ± 10°[8]$^*$              | 57°       |
| $D_e$     | 0.23eV[7]$^*$                 | 0.16eV    |
| $\overline{\mu}$(molec) | 2.10D[9]$^\dagger$ | 2.22D     |

The results for the molecule are shown in table 2. As one can see, the overall agreement with the experimental data is good, the only quantity in error of more than 15% being $\nu_b$. The frequencies $\nu_{ss}$ and $\nu_{as}$ are in the wrong order, a feature common in our potential, but given the small difference between them this does not look too worrying. Attempts made to fix the discrepancy led to an oxygen-oxygen repulsion that is too small.

The numerical results on the dimer are collected in table 3. The ground-state geometry is, qualitatively, the usual one; $\theta_d$ is the angle between the bisector of the H-O-H angle of the donor molecule and the O-O direction, $\theta_a$ is the same for the acceptor. $D_e$ is the dimer dissociation energy.

We found that, as $c_o$ and $R_o$ vary, when the oxygen-oxygen separation increases then $\alpha_o$ decrease by about the same amount, and vice versa: this is clearly an electrostatic effect due to the attraction of the hydrogens in the acceptor.
molecule and the oxygen of the donor molecule. In addition, the angle $\theta_a$ increases, as one would expect, as the molecular dipole moments decrease and tend not to align. The excessive value of $\theta_a$ is therefore a price we have to pay in order to obtain a dipole moment not too high. We also verified that, as $d(O-O)$ increases, $D_e$ decreases. It is thus not surprising that, since $d(O-O)$ is overestimated, $D_e$ is underestimated.

| $\omega$ | Exptl data | Ab-initio (MP2) | This work |
|---------|-------------|----------------|-----------|
| $\omega_{12}$: Donor torsion | - | 141 155 | 107 |
| $\omega_{11}$: Acceptor twist | - | 147 193 | 238 |
| $\omega_8$: Acceptor bend | 243 | 155 178 | 262 |
| $\omega_7$: O-O stretch | 155 | 185 220 | 94 |
| $\omega_6$: In-plane donor wag | 320 | 342 398 | 487 |
| $\omega_{10}$: Out of plane donor bend | 520 | 632 715 | 722 |

**Table 4**

Dimer normal modes (in cm$^{-1}$)

Result for the dimer normal modes are shown in table 4. For their definition we follow Ref.[14] and their identification Refs [10,20,11]. The ordering of the intermolecular frequencies we find is not in complete agreement with experimental or ab initio data; it is the same found by [14], with the exception of the “O-O stretch” mode. The experimental data show that the intramolecular frequencies are not much different from those of the monomer; the main difference consists of an increase of the bending frequencies and a decrease of the symmetric and asymmetric stretching frequencies. These trends, confirmed by ab initio calculations ([14] and [19]), are well reproduced in our results.

The equilibrium geometry of the trimer is shown in fig.1 and the numerical data are collected in table 5. The longest side of the triangle corresponds to the smallest H-bond angle. This is characteristic of our potential. We obtained two relative minima, shown in fig. 2 and 3. The first is 0.06 eV above the energy
in the absolute minimum, the second 0.15 eV. Their ordering in energy is the same as in the \textit{ab initio} calculations [17,18], respectively 0.04 and 0.24 eV.

As an illustration of the overall quality of our potential, in Table 6 we show the trends of two important quantities — the average oxygen-oxygen distance and the average molecular dipole moment — with increasing number \( n \) of molecules in the cluster. To make trends clearer, for \( n < 8 \) the lowest-energy cyclic clusters have been considered, even when they are not the absolute energy minima. It is clear that the trends from \textit{ab initio} calculations are well reproduced and the absolute errors actually decrease with \( n \).

In conclusion, we have shown that the model reproduces the basic physical properties of microclusters in a satisfactory way. In particular, we are able to obtain bond lengths and dipole moments within 10-20\% of experimental and \textit{ab-initio} values, and to reproduce qualitatively not only all the ground-
state geometries, but also several local minima. This remains true when the potential is applied to larger clusters, as we will show in a forthcoming paper. It should be stressed that for almost none of the potentials found in the literature one can find a comparison with experimental or ab-initio data as extensive and thorough as ours. Moreover, the limited number of parameters we used makes it more likely that their values are close to the real ones. We therefore believe that our potential is a promising one with regard to transferability and accuracy.

Table 5
Trimer data aRef.[15],bRef.[14], cHF,dRef.[16], eLDA+GC,fRef.[9].

| Exp. dataa | This work |
|------------|-----------|
| d(O-O)     | 2.94-2.97-2.97Å | 3.10-3.09-3.25Å |
| θ(O₁ - H₃ - O₂) | 152 | 163 |
| θ(O₂ - H₃ - O₃) | 150 | 156 |
| θ(O₃ - H₃ - O₁) | 153 | 164 |
| H₁₄ - (O₁ - O₂ - O₃) | 180 | 175 |
| H₁₅ - (O₂ - O₃ - O₁) | 180 | 180 |
| H₁₆ - (O₃ - O₁ - O₂) | 180 | 181 |

| ab initio | This work |
|-----------|-----------|
| d(O - H)ₖ | 0.977Åc | 0.99-1.00Å |
| d(O - H)ₗ | 0.964Åc | 0.963-0.965-0.966Å |
| Hₖ₁ - (O₁ - O₂ - O₃) | 118e | 93 |
| Hₖ₂ - (O₂ - O₃ - O₁) | 237e | 268 |
| Hₖ₃ - (O₃ - O₁ - O₂) | 231e | 256 |
| Dₑ/N₂mol | 0.22eVc | 0.15eV |
| Dₑ/molec | 2.31Dd | 2.37D |
| Frequency range (cm⁻¹) | | |
| intermolecular | 101-730 b | 75-1083 |
| | 158-863 e | |
| | 185-951 f | |
| intramolecular | 1753-4215 b | 1288-3544 |
| | 1632-3898 e | |
| | 1623-3727 f | |
Fig. 3. Trimer: the next-lowest metastable state

| $n$ | 1 | 2 | 3 | 4 | 6 | 8 |
|-----|---|---|---|---|---|---|
| $d(O-O)(\AA)$ | - | 3.20 | 3.14 | 2.80 | 2.77 |   |
| $d(O-O)(\AA)$ [14] | - | 3.03 | 2.93 | 2.88 | 2.86 |   |
| $\bar{\mu}(molec)(D)$ This work | 2.07 | 2.22 | 2.37 | 2.76 | 2.82 | 2.77 |
| $\bar{\mu}(molec)(D)$ [9] | 1.86 | 2.10 | 2.31 | 2.55 | 2.70 | 2.72 |

Table 6
Trends with varying $n$ in cyclic clusters and the octamer, compared with ab initio results

This work has been funded by a MIUR-COFIN grant.

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