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A first principles polarizable water model for molecular simulations: application to a water dimer

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In this paper we describe a new Hamiltonian model for polarizable water, whose reliability should in principle be independent of system dimension. Such a model is largely based on first principles using the charge density expansion and linear polarizability to treat intermolecular interactions. A semi-empirical function is added only to describe short-range atomic repulsions. The accuracy of this method has been evaluated comparing the results of our model with highly correlated quantum chemical calculations (CCSD(T)) performed on a system of two interacting water molecules. Results show that this model provides a rather accurate description of the system studied.

1. INTRODUCTION

The accurate description of water molecules is a challenging and longstanding topic.[1] A theoretical model for water, both in isolated and condensed state, is of great relevance for the importance of such substance in many chemical and biological processes. Two strategies have been essentially used for modeling water molecules: a detailed electronic description, based on sophisticated quantum-chemical calculations,[2] and a more approximated approach which describes intermolecular interactions in terms of atomic-molecular properties. Although the former can be very accurate, its computational costs are still so heavy to prevent its application to medium-large systems. On the other hand the latter approach, which cannot describe accurately the microscopic details of molecular interactions, is very suited for treating condensed phase conditions. Many of the atomic-molecular models are based on a semi-empirical molecular Hamiltonian[3–6] which in some cases can also include terms for molecular polarizability,[7] and in the last years more theoretically based Hamiltonians have been also proposed.[8–10] All these models are typically

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based on point charges, atomic polarizability in the linear approximation, if present, and simplified short range potentials to describe intermolecular interactions. Such molecular Hamiltonians are efficient in providing many experimental properties, but their description of the pair interaction is not always satisfactory. In the line of these atomic-molecular methods we propose in this paper a new water Hamiltonian based on first physical principles. In our model we still describe many body effects in terms of atomic-molecular polarizability, in the linear approximation, and short range atomic interactions via a simple semi-empirical potential. However, we use an electronic density description beyond the usual atomic point charge approximation, which includes dipole and quadrupole effects, where all the physical parameters involved in the Hamiltonian are obtained by first principles and direct evaluation of observables. This paper is organized as follows: in the first part we describe the theoretical principles underlying the molecular Hamiltonian model, in the second part we will show the results obtained applying such a model to simple system defined by two interacting water molecules; finally we give some conclusions. The aim of the present work is not to describe in details the potential energy surface of a water dimer, but rather to provide a general, physically coherent Hamiltonian for the fluid state, and in particular, for the liquid state.

2. THEORY

2.1. Basic derivations

The water model we propose is based on the following three basic physical approximations:

- The rototranslational degrees of freedom of each molecule are considered completely classical mechanical coordinates, while both the electronic and intramolecular nuclear degrees of freedom (i.e. stretching and bending modes), are considered as quantum mechanical ones;
- For any given rototranslational phase space position of the molecules, we assume that the system is confined in its ground state, i.e. the lowest Hamiltonian eigenstate of the system where all the molecules have fixed rototranslational coordinates and conjugated momenta;
- We also assume that the energy changes of the Hamiltonian ground state as a function of the rototranslational coordinates, defining the Born-Oppenheimer (BO) surface, do not alter the molecule's geometry and hence, classically Speaking, the nuclear intramolecular positions are virtually fixed.

In the case of fluid state water these assumptions are excellent approximations at least up to 700-800 K.

The total energy on the BO surface is then

$$\mathcal{U}(\boldsymbol{x},\boldsymbol{p}) = \mathcal{K}(\boldsymbol{p}) + \mathcal{U}'(\boldsymbol{x}) \quad (1)$$

$$\mathcal{U}'(\boldsymbol{x}) = \left\langle \Psi_0 | \widehat{H} | \Psi_0 \right\rangle \quad (2)$$

where $\boldsymbol{x}$ and $\boldsymbol{p}$ are the rototranslational coordinates and conjugated momenta of the molecules, $\mathcal{K}$ the overall rototranslational kinetic energy that for rigid or semirigid

molecules is a function only of the momenta, $\widehat{H}$ the Hamiltonian operator of the electronic and nuclear intramolecular degrees of freedom at a fixed rototranslational configuration, and Ψ_0 the corresponding ground state eigenfunction. Considering as a reference condition (unperturbed state) an identical system in the same rototranslational phase space position, but with no intermolecular interactions, we have that Eq. 2 can be written as

$$\begin{aligned}
\mathcal{U}'(\boldsymbol{x}) &= \left\langle \Psi_0 | \widehat{H}^0 | \Psi_0 \right\rangle + \left\langle \Psi_0 | \widehat{V} | \Psi_0 \right\rangle \\
&= \mathcal{U}^{0'} + V^0(\boldsymbol{x}) + \Delta\mathcal{U}^{0'}(\boldsymbol{x}) + \Delta V(\boldsymbol{x}) \qquad (3) \\
\mathcal{U}^{0'} &= \left\langle \Psi_0^0 | \widehat{H}^0 | \Psi_0^0 \right\rangle \qquad (4) \\
V^0(\boldsymbol{x}) &= \left\langle \Psi_0^0 | \widehat{V} | \Psi_0^0 \right\rangle \qquad (5) \\
\Delta\mathcal{U}^{0'}(\boldsymbol{x}) &= \left\langle \Psi_0 | \widehat{H}^0 | \Psi_0 \right\rangle - \left\langle \Psi_0^0 | \widehat{H}^0 | \Psi_0^0 \right\rangle \qquad (6) \\
\Delta V(\boldsymbol{x}) &= \left\langle \Psi_0 | \widehat{V} | \Psi_0 \right\rangle - \left\langle \Psi_0^0 | \widehat{V} | \Psi_0^0 \right\rangle \qquad (7)
\end{aligned}$$

where $\widehat{H}^0$ is the unperturbed Hamiltonian operator, $\widehat{V}$ the perturbation operator providing the intermolecular energy and Ψ_0^0 is the unperturbed eigenfunction of the system. From second order perturbation theory[11] we have

$$\Delta\mathcal{U}^{0'} \cong -\frac{\Delta V}{2} \qquad (8)$$

and hence assuming Eq. 8 valid in general

$$\mathcal{U}'(\boldsymbol{x}) \cong \mathcal{U}^{0'} + V^0(\boldsymbol{x}) + \frac{\Delta V}{2} \qquad (9)$$

Note that we describe $\widehat{V}$ only in terms of electric interactions neglecting magnetic and exchange interactions; the former are very weak and the latter must be used only in the case a significant electron mixing between molecules is present. In the condition of interest of this paper, i.e. not very low temperature and fluid state behaviour which does not involve relevant chemical events, magnetic and exchange interactions can be safely disregarded in the Hamiltonian. The three terms in Eq. 9 can be evaluated as follows. The first term $\mathcal{U}^{0'}$ is simply the Hamiltonian ground state eigenvalue for the unperturbed system which is independent of the coordinates $\boldsymbol{x}$ and given by the vibroelectronic ground state of an isolated molecule. The second term $V^0(\boldsymbol{x})$, providing the intermolecular energy due to the unperturbed molecular charge distribution, can be approximated expanding the oxygen and hydrogens charge distributions up to the quadrupoles. Finally the last term, $\Delta V(\boldsymbol{x})$, provides the interaction energy shift due to the molecular polarizability, and is approximated in our model expanding the variation of the molecular charge distribution up to the dipoles. Such approximations are clearly not valid at short intermolecular distance where the higher order energy terms become relevant. In our model, as it will be shown, we treat such short range interactions via a semi-empirical energy term (Buckingham potential) which in principle includes all the energy terms disregarded in the expansions mentioned above.

In order to evaluate the unperturbed atomic charges, dipoles and quadrupoles we made the reasonable assumption that the hydrogen unperturbed dipole and quadrupole are virtually zero. In figure 1 we show a water molecule, in the unperturbed vibroelectronic ground state, in the molecular reference frame, centered in the molecular center of mass, which diagonalizes the molecular quadrupole matrix.

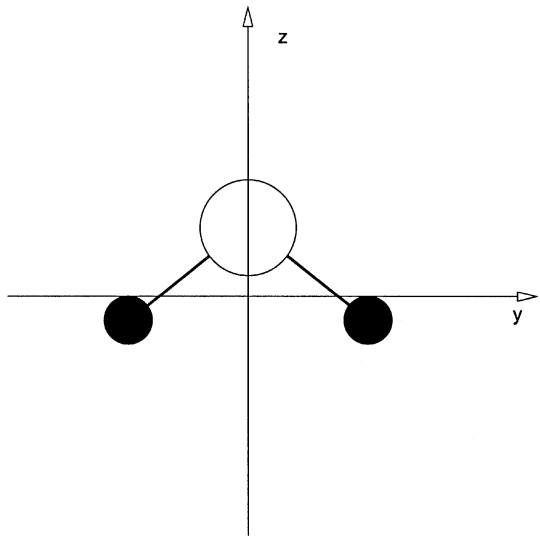

Figure 1. Water molecule in the molecular reference frame that diagonalizes the molecular quadrupole matrix, centered in the molecular center of mass. The water geometry used is defined in table 1 as well as in the text.

We can easily set a system of equations which can be used to evaluate the unperturbed atomic charges (q_{H1}, q_{H2}, q_O), the unperturbed oxygen dipole ($\mu^0_{Ox}, \mu^0_{Oy}, \mu^0_{Oz}$), and the unperturbed (diagonal) oxygen quadrupole elements ($Q^0_{Oxx}, Q^0_{Oyy}, Q^0_{Ozz}$). Note that the atomic dipole and quadrupole are defined using as origin of the charges coordinates the nuclear position. In fact, from the molecular charge, dipole and

quadrupole, and using the definition of dipole and quadrupole we have

$$
\begin{aligned}
0 &= q_{H1} + q_{H2} + q_O && (10)\\
\mu_x^0 &= \mu_{Ox}^0 = 0 && (11)\\
\mu_y^0 &= \mu_{Oy}^0 = 0 && (12)\\
\mu_z^0 &= z_{H1}q_{H1} + z_{H2}q_{H2} + z_O q_O + \mu_{Oz}^0 && (13)\\
Q_{xx}^0 &= Q_{Oxx}^0 && (14)\\
Q_{yy}^0 &= q_{H1}y_{H1}^2 + q_{H2}y_{H2}^2 + Q_{Oyy}^0 && (15)\\
Q_{zz}^0 &= q_{H1}z_{H1}^2 + q_{H2}z_{H2}^2 + q_O z_O^2 + 2z_O\mu_{Oz}^0 + Q_{Ozz}^0 && (16)\\
q_{H1} &= q_{H2} = q_H && (17)
\end{aligned}
$$

with $\mu_x^0, \mu_y^0, \mu_z^0, Q_{xx}^0, Q_{yy}^0, Q_{zz}^0$ the unperturbed molecular dipole and quadrupole components and the atomic coordinates given by the corresponding nuclear positions.

Table 1
Parameters of the model and input molecular properties used. Unperturbed molecular, $\boldsymbol{\mu}^0$, and oxygen, $\boldsymbol{\mu}_O^0$, dipole moments are along the z-axis defined in figure 1, and hence we give in the table only their z components. Note that $\widetilde{Q}^0$ is the unperturbed molecular quadrupole matrix.

property	value
d(O-H)	0.96 Å
angle(HOH)	105.00 degrees
q_O	-1.185 a.u.
q_H	0.5925 a.u.
B_O	10.254999 a.u.
C_O	1.4376648 a.u.
B_H	3.3899 a.u.
C_H	1.79039 a.u.
$Tr(\widetilde{\alpha})/3$	9.94 a.u.
μ_z^0	-2.141059 D
μ_{Oz}^0	1.059 D
$Tr(\widetilde{Q}^0)/3$	-4.66 a.u.

The previous 8 equations are insufficient to solve the 9 parameters needed, hence we used a further approximation $Q_{Oxx}^0 \cong Q_{Oyy}^0$ in order to obtain all the atomic parameters. Interestingly, solving such nine equations we obtained rather similar oxygen quadrupole (diagonal) elements (maximum relative shift about 14%). This means that the unperturbed oxygen quadrupole is nearly degenerate and hence its effects on the interaction energy are not relevant, except at very short intermolecular distances. We can then simplify our derivation, keeping an accurate description of

the interaction energy, considering the unperturbed oxigen quadrupole as really degenerate, i.e. $Q^0_{Oxx} = Q^0_{Oyy} = Q^0_{Ozz}$.

2.2. Energy of the unperturbed charge distribution

Using the general electro-magnetic theory we can express $V^0(\boldsymbol{x})$ as follows

$$V^0(\boldsymbol{x}) = \sum_i \sum_{j>i} \sum_{l_i} \sum_{l_j} \int_{l_j} \Phi^0_{l_i}(\boldsymbol{r}) \rho^0_{l_j}(\boldsymbol{r}) d\boldsymbol{r} \tag{18}$$

where i and j refer to the molecules, l_i and l_j to the atoms of the molecules i and j respectively, $\Phi^0_{l_i}$ is the unperturbed electric potential due to the l_i atom and felt at a given position in the l_j atom region, $\rho^0_{l_j}$ is the unperturbed charge density in atom l_j, the position vector $\boldsymbol{r}$ is taken with respect to the laboratory frame, and finally the integral subscript means that the integration is taken only over the space in the l_j atom region. Note that in the previous equation we omitted the implicit dependence of $\Phi^0_{l_i}$ and $\rho^0_{l_j}$ on the rototranslational coordinates $\boldsymbol{x}$. If in the previous equation we expand the electric potential around the l_j atom nuclear position $\boldsymbol{r}_{N_{l_j}}$ up to the second order

$$\begin{aligned}
\Phi^0_{l_i}(\boldsymbol{r}) &\cong \Phi^0_{l_i}(\boldsymbol{r}_{N_{l_j}}) + \boldsymbol{\nabla}\Phi^0_{l_i}(\boldsymbol{r}_{N_{l_j}}) \cdot (\boldsymbol{r} - \boldsymbol{r}_{N_{l_j}}) + (\boldsymbol{r} - \boldsymbol{r}_{N_{l_j}})^T \frac{\widetilde{A}_{l_i}(\boldsymbol{r}_{N_{l_j}})}{2} (\boldsymbol{r} - \boldsymbol{r}_{N_{l_j}}) \\
A^{k,k'}_{l_i} &= \left(\frac{\partial^2 \Phi^0_{l_i}}{\partial r_k \partial r_{k'}} \right)_{\boldsymbol{r}=\boldsymbol{r}_{N_{l_j}}}
\end{aligned}$$

we obtain, after some algebra

$$V^0(\boldsymbol{x}) \cong \sum_i \sum_{j>i} \sum_{l_i} \sum_{l_j} \left[\Phi^0_{l_i} q_{l_j} + \boldsymbol{\nabla}\Phi^0_{l_i}(\boldsymbol{r}_{N_{l_j}}) \cdot \boldsymbol{\mu}^0_{l_j} + \frac{1}{2} \sum_{k=1}^{3} \sum_{k'=1}^{3} A^{k,k'}_{l_i} Q^{0k,k'}_{l_j} \right] \tag{19}$$

where

$$q_{l_j} = \int_{l_j} \rho^0_{l_j}(\boldsymbol{r}) d\boldsymbol{r} \tag{20}$$

$$\boldsymbol{\mu}^0_{l_j} = \int_{l_j} \rho^0_{l_j}(\boldsymbol{r})(\boldsymbol{r} - \boldsymbol{r}_{N_{l_j}}) d\boldsymbol{r} \tag{21}$$

$$Q^{0k,k'}_{l_j} = \int_{l_j} \rho^0_{l_j}(\boldsymbol{r})(r_k - r^k_{N_{l_j}})(r_{k'} - r^{k'}_{N_{l_j}}) d\boldsymbol{r} \tag{22}$$

are the total charge, the unperturbed dipole (electric moment) and the k, k' element of the unperturbed quadrupole moment of l_j atom, respectively. Furthermore we can also expand the electric potential in terms of the l_i atom charge distribution, again up to the quadrupole

$$\begin{aligned}
\Phi^0_{l_i}(\boldsymbol{r}_{N_{l_j}}) &\cong K_{el} \frac{q_{l_i}}{|\boldsymbol{r}_{N_{l_j}} - \boldsymbol{r}_{N_{l_i}}|} + K_{el} \frac{\boldsymbol{\mu}^0_{l_i} \cdot [\boldsymbol{r}_{N_{l_j}} - \boldsymbol{r}_{N_{l_i}}]}{|\boldsymbol{r}_{N_{l_j}} - \boldsymbol{r}_{N_{l_i}}|^3} \\
&+ \frac{K_{el}}{2} \sum_{k=1}^{3} \sum_{k'=1}^{3} Q^{0k,k'}_{l_i} \left[\frac{3 \left(r^k_{N_{l_j}} - r^k_{N_{l_i}} \right) \left(r^{k'}_{N_{l_j}} - r^{k'}_{N_{l_i}} \right)}{|\boldsymbol{r}_{N_{l_j}} - \boldsymbol{r}_{N_{l_i}}|^5} - \frac{\delta_{k,k'}}{|\boldsymbol{r}_{N_{l_j}} - \boldsymbol{r}_{N_{l_i}}|^3} \right]
\end{aligned}$$

with $K_{el} = 1/(4\pi\epsilon_0)$ and $\delta_{k,k'}$ the Kroenecker's delta. As mentioned above, in our model we consider the unperturbed hydrogen quadrupole and dipole to be zero and the unperturbed oxygen quadrupole to be degenerate, i.e. the quadrupole matrix is diagonal with three identical eigenvalues. With such an approximation and inserting in Eq. 19 the matrix $\widetilde{A}_{l_i}$ elements we obtain, disregarding the terms proportional to $1/|\boldsymbol{r}_{N_{l_j}} - \boldsymbol{r}_{N_{l_i}}|^n$ with $n > 3$,

$$
\begin{aligned}
V^0(\boldsymbol{x}) \cong & \sum_i \sum_{j>i} \sum_{l_i} \sum_{l_j} K_{el} \left[\frac{q_{l_i} q_{l_j}}{|\boldsymbol{r}_{N_{l_j}} - \boldsymbol{r}_{N_{l_i}}|} \right. \\
& + \frac{q_{l_j}\, \boldsymbol{\mu}^0_{l_i} \cdot [\boldsymbol{r}_{N_{l_j}} - \boldsymbol{r}_{N_{l_i}}]}{|\boldsymbol{r}_{N_{l_j}} - \boldsymbol{r}_{N_{l_i}}|^3} - \frac{q_{l_i}\, \boldsymbol{\mu}^0_{l_j} \cdot [\boldsymbol{r}_{N_{l_j}} - \boldsymbol{r}_{N_{l_i}}]}{|\boldsymbol{r}_{N_{l_j}} - \boldsymbol{r}_{N_{l_i}}|^3} \\
& + \frac{\boldsymbol{\mu}^0_{l_i} \cdot \boldsymbol{\mu}^0_{l_j}}{|\boldsymbol{r}_{N_{l_j}} - \boldsymbol{r}_{N_{l_i}}|^3} \\
& - \left. 3 \frac{\boldsymbol{\mu}^0_{l_i} \cdot [\boldsymbol{r}_{N_{l_j}} - \boldsymbol{r}_{N_{l_i}}]\ \boldsymbol{\mu}^0_{l_j} \cdot [\boldsymbol{r}_{N_{l_j}} - \boldsymbol{r}_{N_{l_i}}]}{|\boldsymbol{r}_{N_{l_j}} - \boldsymbol{r}_{N_{l_i}}|^5} \right]
\end{aligned}
\tag{23}
$$

Note that the last equation cannot be valid at short interatomic distances where the higher order energy terms, disregarded in Eqs 19 and 23, become relevant.

2.3. Polarizability effects

For a given rototranslational configuration, in our model, molecular polarization results from the effect of the electric field due to the other molecules and can be treated, disregarding higher order effects, i.e. hyperpolarizabilities, via the molecular polarizability matrix $\widetilde{\alpha}$, defined at zero electric field,

$$
\boldsymbol{\mu}_i - \boldsymbol{\mu}^0_i \cong \widetilde{\alpha}_i \sum_j \boldsymbol{E}_j \tag{24}
$$

where the i subscript refers to the i-th molecule and $\boldsymbol{E}_j$ is the electric field felt by the i-th molecule due to the j-th one. Note that in the previous equation the j index is never equal to i. In Eq. 9 the only term due to such molecular polarizability is ΔV which is the energy difference between the actual interaction, including the polarizability, and the interaction energy only due to the stationary unperturbed charge distribution. Such a term, which includes the dispersion energy (dipole-induce dipole interactions), is small for most of the configurations in our BO surface and hence, for not too short intermolecular distances, it could be approximated using only dipolar terms

$$
\Delta V \cong -\sum_i \left(\boldsymbol{\mu}_i \cdot \sum_{j>i} \boldsymbol{E}_j - \boldsymbol{\mu}^0_i \cdot \sum_{j>i} \boldsymbol{E}^0_j \right) \tag{25}
$$

$$
\boldsymbol{E}_j \cong -\frac{\boldsymbol{\mu}_j}{|\boldsymbol{r}_{G_j} - \boldsymbol{r}_{G_i}|^3} + 3 \frac{\boldsymbol{\mu}_j \cdot (\boldsymbol{r}_{G_j} - \boldsymbol{r}_{G_i})}{|\boldsymbol{r}_{G_j} - \boldsymbol{r}_{G_i}|^5} (\boldsymbol{r}_{G_j} - \boldsymbol{r}_{G_i}) \tag{26}
$$

$$
\boldsymbol{E}^0_j \cong -\frac{\boldsymbol{\mu}^0_j}{|\boldsymbol{r}_{G_j} - \boldsymbol{r}_{G_i}|^3} + 3 \frac{\boldsymbol{\mu}^0_j \cdot (\boldsymbol{r}_{G_j} - \boldsymbol{r}_{G_i})}{|\boldsymbol{r}_{G_j} - \boldsymbol{r}_{G_i}|^5} (\boldsymbol{r}_{G_j} - \boldsymbol{r}_{G_i}) \tag{27}
$$

where $\boldsymbol{r}_{G_j}, \boldsymbol{r}_{G_i}$ are the positions of the j-th and i-th molecular centers of mass. Combining now Eqs 26 and 24 we obtain, using the matrix notation,

$$\boldsymbol{\mu}_i - \boldsymbol{\mu}_i^0 \cong \widetilde{\alpha}_i \sum_j \widetilde{D}_{j,i} \boldsymbol{\mu}_j \tag{28}$$

$$D_{j,i}^{k,k'} = 3\frac{(r_{G_j}^k - r_{G_i}^k)(r_{G_j}^{k'} - r_{G_i}^{k'})}{|\boldsymbol{r}_{G_j} - \boldsymbol{r}_{G_i}|^5} - \frac{\delta_{k,k'}}{|\boldsymbol{r}_{G_j} - \boldsymbol{r}_{G_i}|^3} \tag{29}$$

From the last equations, defining with $\boldsymbol{\mu}$ and $\boldsymbol{\mu}^0$ the multidimensional vectors of the actual and unperturbed molecular dipoles, we have

$$\boldsymbol{\mu} \cong \boldsymbol{\mu}^0 + \widetilde{\Theta}\boldsymbol{\mu} \tag{30}$$

where if N is the total number of molecules, $\boldsymbol{\mu}$ and $\boldsymbol{\mu}^0$ are $3N$ dimensional vectors and $\widetilde{\Theta}$ is a $3N \times 3N$ matrix defined as

$$\widetilde{\Theta} = \begin{pmatrix} \widetilde{\theta}_{1,1} & \widetilde{\theta}_{1,2} & ..... & \widetilde{\theta}_{1,N} \\ \widetilde{\theta}_{2,1} & \widetilde{\theta}_{2,2} & ..... & \widetilde{\theta}_{2,N} \\ ..... & ..... & ..... & ..... \\ ..... & ..... & ..... & ..... \\ \widetilde{\theta}_{N,1} & \widetilde{\theta}_{N,2} & ..... & \widetilde{\theta}_{N,N} \end{pmatrix} \tag{31}$$

which the diagonal 3×3 matrices $\widetilde{\theta}_{i,i}$ are always zero elements matrices and $\widetilde{\theta}_{i,j} = \widetilde{\alpha}_i \widetilde{D}_{j,i}$. Eq. 30 can be easily solved by inversion

$$\boldsymbol{\mu} \cong \left(\widetilde{I} - \widetilde{\Theta}\right)^{-1} \boldsymbol{\mu}^0 \tag{32}$$

providing at each BO surface position the molecular dipoles which can be used into Eq. 25 in order to obtain the energy term $\Delta V(\boldsymbol{x})$. Note that Eq. 32 provides good estimates of the perturbed molecular dipoles only for polar molecules where the non linear effects of the perturbing field are rather small compared to the linear ones. For apolar molecules, on the contrary, such hyperpolarizability effects become very relevant and hence cannot be properly treated by Eq. 24 which disregards any non linear dependence.

2.4. Short range interatomic interactions

In the previous subsections we derived very general expressions to approximate V^0 and ΔV making use only of basic physical mathematical principles. However, these expressions are not accurate at short interatomic distances where the energy terms disregarded in Eqs 19, 23 and 25, become relevant. Hence, to construct an accurate model which can treat also short range interactions we must include an extra energy term. In this paper we model this term using a repulsive Buckingham potential to describe the short range oxygen and hydrogen interactions. Such semi-empirical potential is widely used as it is rather accurate and any more "rigorous" derivation is very difficult and computationally demanding. We can then rewrite Eq. 9 as

$$\mathcal{U}'(\boldsymbol{x}) - \mathcal{U}^{0'} \cong \mathcal{U}'_I(\boldsymbol{x}) + \frac{\mathcal{U}'_{II}(\boldsymbol{x})}{2} + \mathcal{U}'_{SR}(\boldsymbol{x}) \tag{33}$$

where

$$\mathcal{U}'_I(\boldsymbol{x}) = \sum_i \sum_{j>i} \sum_{l_i} \sum_{l_j} K_{el} \left[\frac{q_{l_i} q_{l_j}}{|\boldsymbol{r}_{N_{l_j}} - \boldsymbol{r}_{N_{l_i}}|} + \frac{q_{l_j}\, \boldsymbol{\mu}^0_{l_i} \cdot [\boldsymbol{r}_{N_{l_j}} - \boldsymbol{r}_{N_{l_i}}]}{|\boldsymbol{r}_{N_{l_j}} - \boldsymbol{r}_{N_{l_i}}|^3} - \frac{q_{l_i}\, \boldsymbol{\mu}^0_{l_j} \cdot [\boldsymbol{r}_{N_{l_j}} - \boldsymbol{r}_{N_{l_i}}]}{|\boldsymbol{r}_{N_{l_j}} - \boldsymbol{r}_{N_{l_i}}|^3} + \frac{\boldsymbol{\mu}^0_{l_i} \cdot \boldsymbol{\mu}^0_{l_j}}{|\boldsymbol{r}_{N_{l_j}} - \boldsymbol{r}_{N_{l_i}}|^3} - 3\frac{\boldsymbol{\mu}^0_{l_i} \cdot [\boldsymbol{r}_{N_{l_j}} - \boldsymbol{r}_{N_{l_i}}]\ \boldsymbol{\mu}^0_{l_j} \cdot [\boldsymbol{r}_{N_{l_j}} - \boldsymbol{r}_{N_{l_i}}]}{|\boldsymbol{r}_{N_{l_j}} - \boldsymbol{r}_{N_{l_i}}|^5} \right] \tag{34}$$

$$\mathcal{U}'_{II}(\boldsymbol{x}) = -\sum_i \left(\boldsymbol{\mu}_i \cdot \sum_{j>i} \boldsymbol{E}_j - \boldsymbol{\mu}^0_i \cdot \sum_{j>i} \boldsymbol{E}^0_j \right) \tag{35}$$

$$\mathcal{U}'_{SR}(\boldsymbol{x}) = \sum_i \sum_{j>i} \sum_{l_i} \sum_{l_j} B_{l_i} B_{l_j} e^{-C_{l_i} C_{l_j} |\boldsymbol{r}_{N_{l_j}} - \boldsymbol{r}_{N_{l_i}}|} \tag{36}$$

and in Eq. 35 $\boldsymbol{\mu}_i$ and $\boldsymbol{E}_j$ are given according to the previous subsection. Note also that in the short range Buckingham potential, $\mathcal{U}'_{SR}$, there are only four adjustable parameters (two for the oxygen and two for the hydrogen) since we only used repulsive interactions as the short range attractive ones should be largely involved in Eq. 35 (i.e. induced dipole-induced dipole interaction).

3. QUANTUM CHEMICAL CALCULATIONS

Water dimer represents a challenging aspect of quantum chemistry.[12–15] Several studies have indeed demonstrated that only with highly correlated methods and with the use of very large atomic basis sets, a reliable description of the intermolecular interaction can be obtained.[16] Anyhow, even when very accurate calculations are carried out, the basis set superposition error (BSSE) still represents a further limitation whose solution is still at the centre of substained interest.[17] In the light of these well known warnings, we decided to adopt for our reference calculations, the highly correlated coupled cluster theory in its standard implementation which includes all the single and double excitations with a non iterative inclusion of the triples.[18] The Pople's triple zeta with diffuse and polarization functions 6-311+g(d,p)[19] basis set has been chosen. The BSSE effect was then added through the counterpoise method of Boys and Bernardi.[20] In the dimer calculations the two molecules were kept at a fixed geometry consisting of an OH distance of 0.96 $\AA$ and a valence angle of 105.0 degrees. The quantum chemical results we obtained were in good agreement with literature quantum chemical data, i.e. energy and Oxygen-Oxygen distance in the H-bond configuration.[21] Also the dipole moment of the isolated monomer was calculated at the CCSD(T) / 6-311+g(d,p) level of theory and resulted as large as 2.1 Debye, about 0.2 Debye larger than the experimental one.[22] On the other hand, the polarizability tensor, determined at the same level, showed diagonal elements as large as 9.52, 9.85 and 10.32 a.u. in good agreement with the experimental values.[23] All these calculations were done using Gaussian 98 package DEC-AIXP-OSF

version, revision A.7.[24]

4. RESULTS

In the present paper we limit our attention to the energy of the water dimer according to different relative positions of the monomers. However, as already remarked in the introduction, the method is absolutely general and its extension to medium to large sized water clusters is presently under investigation. The Hamiltonian model, presented in this paper, was obtained as follows:

- High level, i.e. highly correlated, quantum chemical calculations were carried out in order to obtain the BO surface energy of the different relative orientations of the water dimer used, as reported in figures 2-6.
- For the same orientations $\mathcal{U}'_I$ and $\mathcal{U}'_{II}$ terms, described in the Theory section, were evaluated.
- The short range atomic repulsive interaction of oxygen and hydrogens, modeled using the semi-empirical potential $\mathcal{U}'_{SR}$, was parametrized fitting the energy difference between the free quantum chemical calculation and the energy obtained summing $\mathcal{U}'_I$ and $\mathcal{U}'_{II}$, for two different dimer orientations reported in figures 2 and 3.
- The complete "force field" was finally tested by comparing the calculated model energy with the quantum-mechanical curves, for all the dimer orientations.

The theta matrix was built up using the atomic charges, the dipole moment and the polarizability tensor, reported in table 1 together with the four parameters of the Buckingham function. Such a matrix was inverted using a standard procedure as implemented in the LAPACK library.

The results concerning the dimer interaction energy are reported in the a panels of figures 2-6, where the orientations considered are shown below each panel a. Here the CCSD(T) curves, indicated with circles, are compared to the present model, shown by a solid line. The values above 0.1 a.u. were always skipped out by the figure since such values, hardly reached during molecular simulations of water in fluid state at thermal regimes, are out of the interest of the present work. The agreement is always very good also for the three orientations not used in the parametrization, figures 4-6(a), and it is rather remarkable that the 'perpendicular' hydrogen-bond curve, figure 4(a), is also accurately reproduced. The maximum errors never exceed 10^{-3} a.u., see figure 5(a), and the Hamiltonian model reproduces accurately the curves shape. Note that the effects of the short range potential become negligible from about $4 - 5\mathring{A}$ and hence beyond such a distance the energy of the model is only due to the terms derived from first principles. Finally in the b panels we show the dipole shift of the dimer due to the polarizability, i.e. the dipole difference between the actual dimer and two water molecules with the same orientation but not interacting. In the figures the CCSD(T) results are compared with the values obtained using our model, in the same orientations and distance range used in a

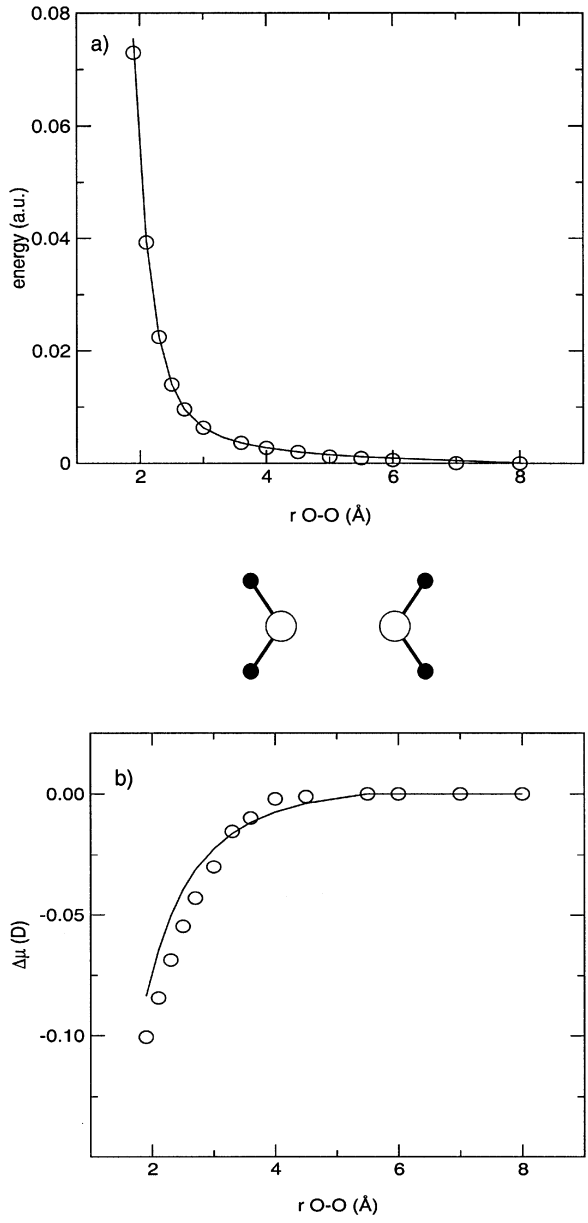

Figure 2. Oxygen repulsive orientation of coplanar water molecules. In the figure are shown the energy interaction (panel a) and $\Delta\mu$ (panel b) at different Oxygen-Oxygen distances. CCSD(T) values are shown by circles and our model's values by a solid line.

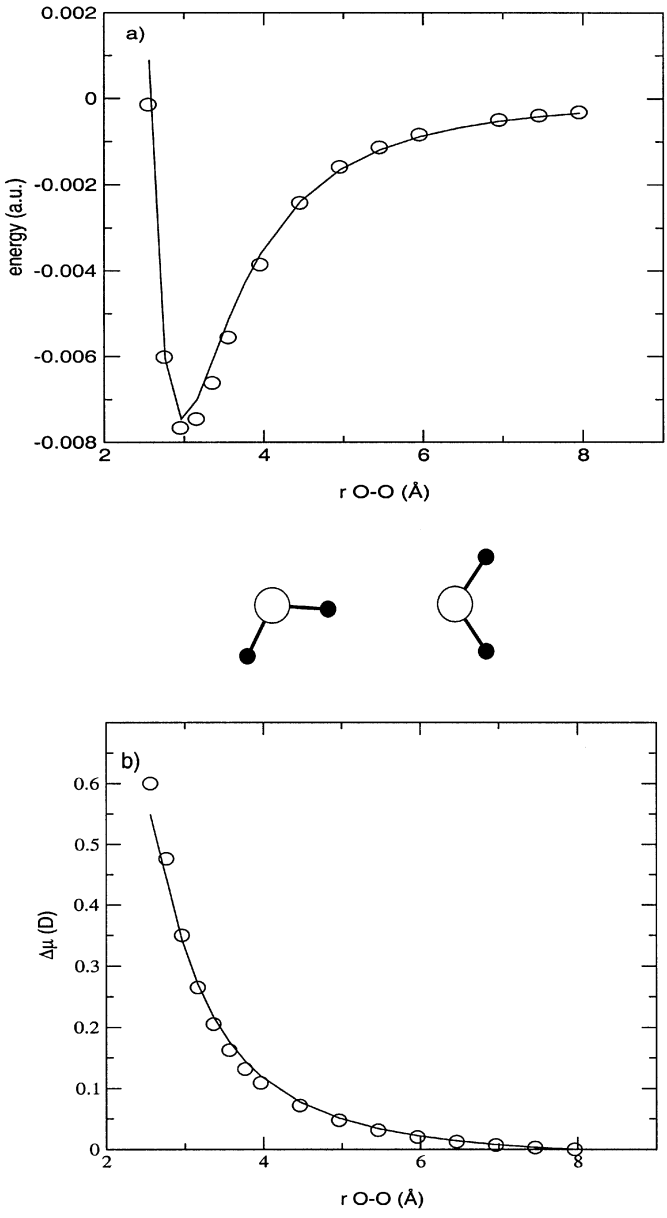

Figure 3. Oxygen attractive orientation of coplanar water molecules. In the figure are shown the energy interaction (panel a) and $\Delta\mu$ (panel b) at different Oxygen-Oxygen distances. CCSD(T) values are shown by circles and our model's values by a solid line.

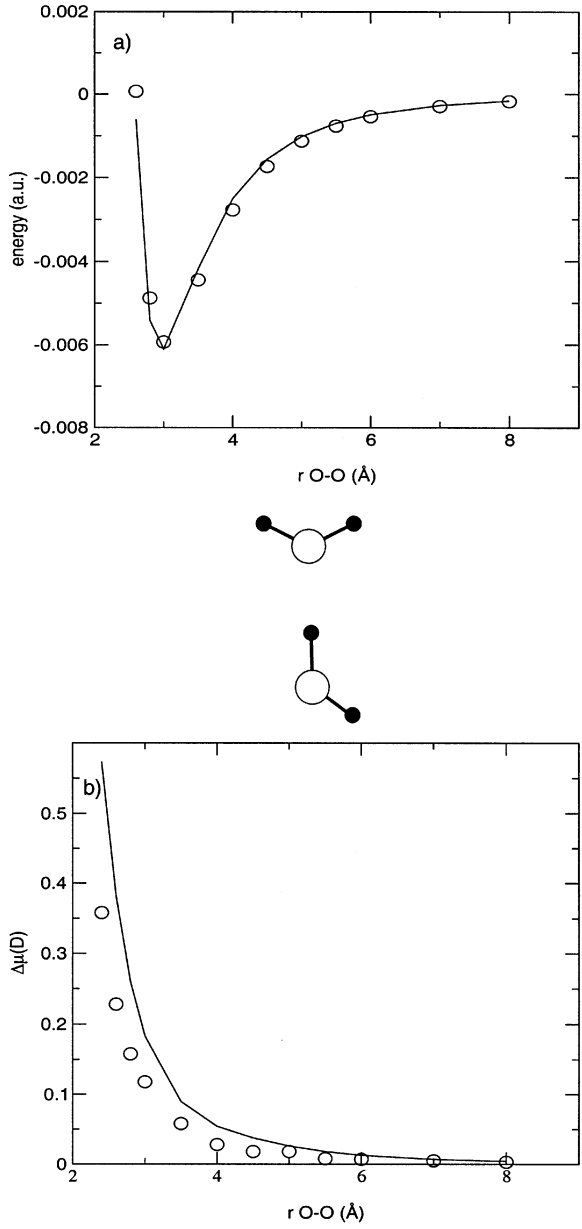

Figure 4. Perpendicular attractive orientation (the H-donor is orthogonal to the acceptor water molecule plane). In the figure are shown the energy interaction (panel a) and $\Delta\mu$ (panel b) at different Oxygen-Oxygen distances. CCSD(T) values are shown by circles and our model's values by a solid line.

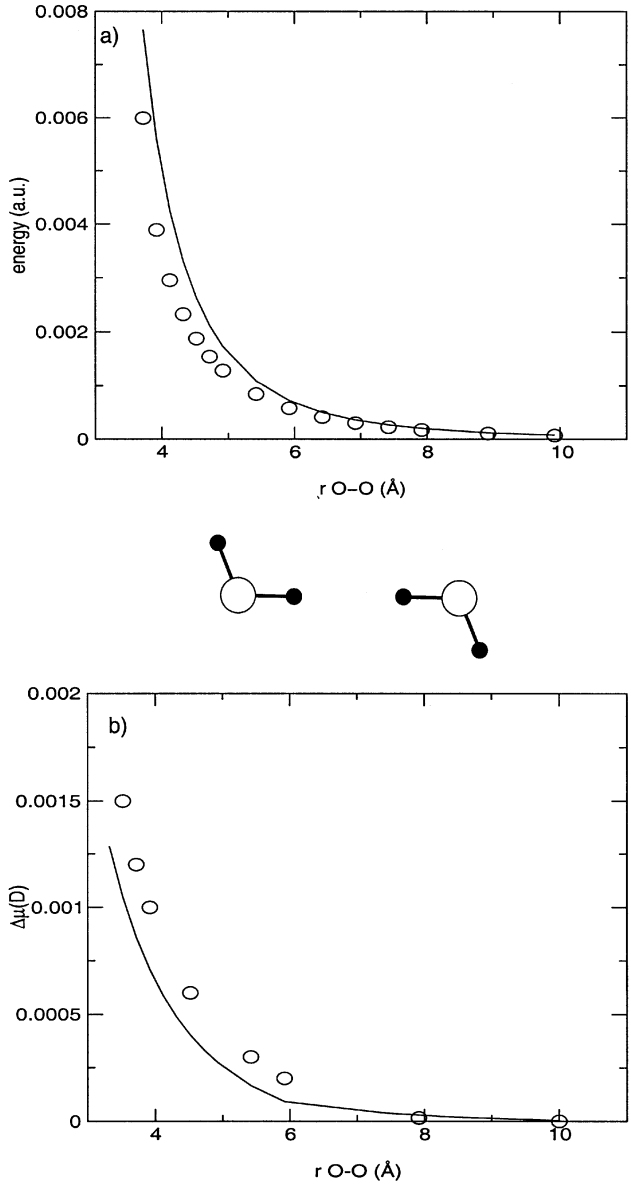

Figure 5. Hydrogen repulsive orientation. In the figure are shown the energy interaction (panel a) and $\Delta\mu$ (panel b) at different Oxygen-Oxygen distances. CCSD(T) values are shown by circles and our model's values by a solid line.

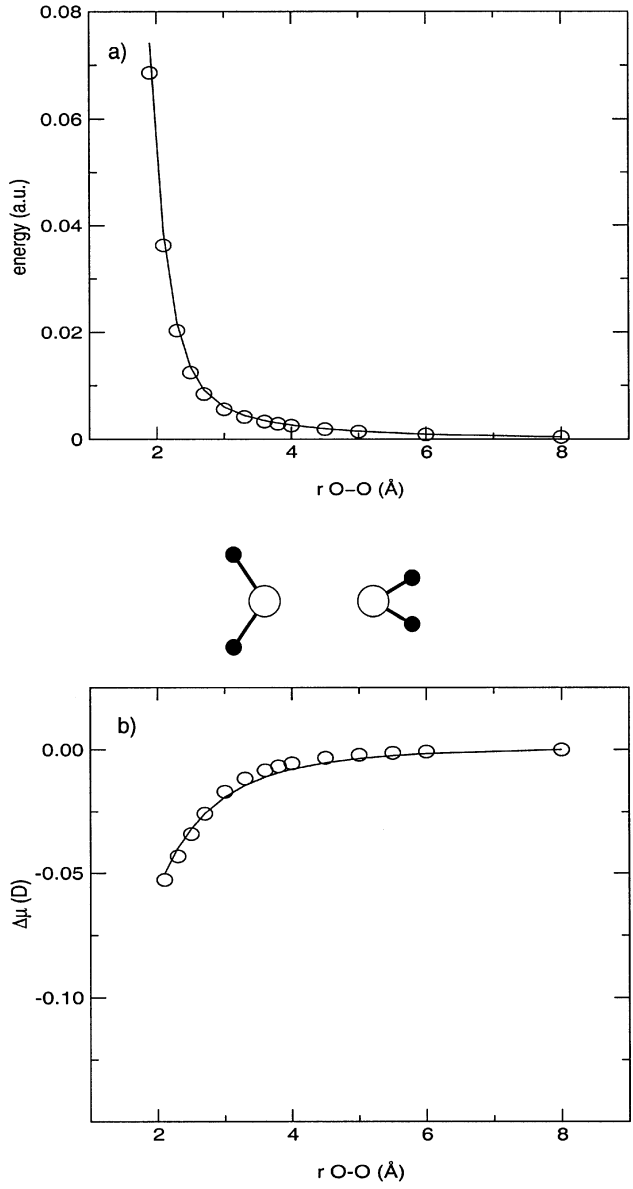

Figure 6. Perpendicular Oxygen repulsive orientation. In the figure are shown the energy interaction (panel a) and $\Delta\mu$ (panel b) at different Oxygen-Oxygen distances. CCSD(T) values are shown by circles and our model's values by a solid line.

panels. The agreement is rather good also for this observable which was not used in the parametrization, and hence such a result shows that the induction effects are well reproduced by the model. Finally the different energy components, defined in the Hamiltonian, have been compared and the results concerning the dimerization orientation are reported in figure 7.

Not surprisingly, the charge-charge term is quantitatively important at whatever oxygen-oxygen distance and the polarization one, up to $3.0\mathring{A}$, approximatively accounts for the $5 - 10\%$ of the overall interaction energy. More interestingly is, on the other hand, the role played by the dipole-charge term which, although resulting very relevant even at long distances, is mostly neglected in the common molecular force fields.

5. CONCLUSIONS

In this article we propose a new molecular Hamiltonian for water which is essentially derived from first principles, with only the short range atomic repulsion described by a semi-empirical function. Using charge density expansion up to atomic quadrupole and molecular polarizability in the linear approximation, our model can reproduce with high accuracy both the interaction energy as well as the total dipole moment of a water dimer, in different orientations and distances, as obtained by sophisticated quantum chemical calculations. The results presented suggest that this model can be very efficient in the simulation of liquid water and in particular for simulating complex solute-solvent systems, such as solvated biological macromolecules, ions, etc.. It is also worth noting that a reliable polarizable water model can be essential for treating quantum mechanical centers in a classical environment, e.g. QM/MM approaches. Finally such a model could be of great relevance for performing accurate predictions on water thermodynamics and statistical mechanics, which are currently under investigation in our groups.

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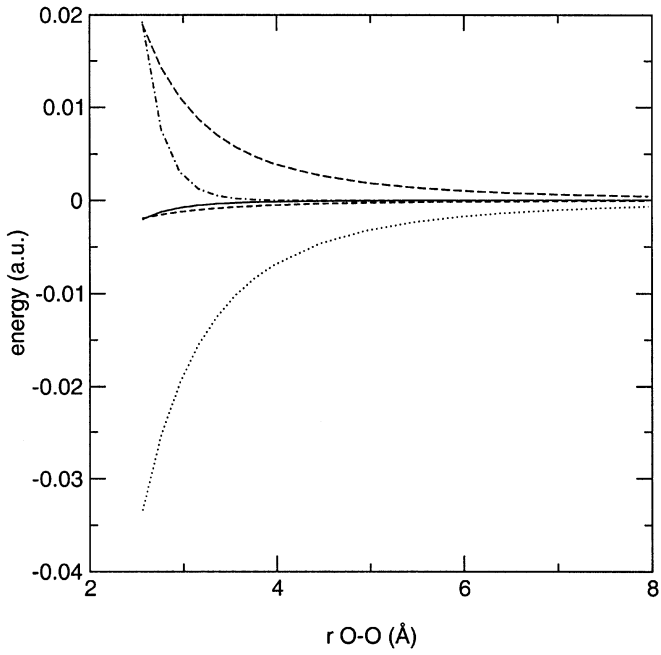

Figure 7. Energy components calculated for the dimerization orientation according to the molecular Hamiltonian model: charge-charge (dotted), polarization (solid line), dipole-dipole (dashed), dipole-charge (long dashed) and Buckingham (dotted-dashed).

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