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Theoretical characterization of structural and energetical properties of water clusters, by means of a simple polarizable water Hamiltonian

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1. Introduction

Water is by far the most widely studied system. The reason of this interest is due to its ubiquity in our environment. Thus the main goal of physics and chemistry of water is to understand and, by simulations, to reproduce the behavior of water properties (e.g. heat capacities, density, dielectric constant etc.) over a wide range of thermodynamic conditions. However, despite the large amount of theoretical and experimental efforts, an accurate description of water behavior from gas to liquid phase still remains an open problem.

Computational modelling at atomic level is obtained through the knowledge of the Potential Energy Surface (PES) and its gradients as a function of the atomic positions. Empirical potentials optimized for liquid water have a simple analytic form providing a high computational efficiency in molecular simulations. However, although they typically reproduce properly the main thermodynamic properties of liquid water, they are unable to provide an accurate description of atomic-molecular interactions for conditions far from the range of parameterization.

On the other hand, in the ab initio approaches, very sophisticated quantum chemical calculations are performed in order to describe in details the true intermolecular PES. Nevertheless, given the computational cost of the ab initio calculations, such PES can be constructed

ABSTRACT

In a previous paper we introduced a new Hamiltonian model for polarizable water, based on the atomic charge density expansion, whose reliability should in principle be independent of the system conditions. In this work we refine and apply this model to describe the structural and energetical features of clusters of increasing dimension and to evaluate the second virial coefficient. Results show that, despite its simplicity, such Hamiltonian provides an efficient and rather accurate description of the systems studied.

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only for small molecular clusters and extrapolations of such Hamiltonians to condensed phase is typically unsatisfactory because the computational cost becomes prohibitive as the system size becomes large as required by liquid state simulations.

The SPC [1] and the TIP4P [2] potentials are the most commonly used empirical models for simulating liquid water, due to their simplicity, low computational cost and good reproduction of the main liquid water features. Both these rigid non-polarizable models incorporate a single Lennard-Jones interaction site and three fixedcharge sites representing the molecular charge distribution in condensed state. These effective pair-potentials are typically parameterized to reproduce the main structural features of liquid water, the enthalpy of vaporization, and the diffusion coefficient at ambient conditions. One major shortcoming of these simple models is that polarization effects are not explicitly included and hence, they can be inaccurate to reproduce thermodynamic and kinetic properties of water over a large range of temperaturedensity states.

For this reason a large effort has been made in recent years to introduce the polarization effect in water molecular potentials using different approaches. However such polarizable models, which should be in principle accurate from gas to liquid state conditions, are based on a complex force field with a high number of parameters and often utilize a virtual molecular model making use of nonphysical energy terms. Here we briefly recall the most recently developed ones.

In the MCDHO [3] model, the polarization is included by means of a virtual harmonic oscillator potential that binds a mobile negative charge to the oxygen.

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Table 1

Parameters of the SPW model and input molecular properties used

Property	Value
d _{O-H}	0.98 Å
HÔH	105.00
qo	–1.185 a.u.
$q_{\rm H}$	0.5925 a.u.
$Tr(\tilde{\alpha})/3$	9.94 a.u.
μ_z^0	-2.141059 D
μ_{Oz}^0	1.059 D
$Tr(\tilde{Q}^{0})/3$	-4.66 a.u.
Bo	7.85353 a.u.
Co	1.38588 a.u.
B _H	4.49677 a.u.
C _H	1.88859 a.u.

In our reference frame [7], the unperturbed molecular μ^0 and oxygen μ_0^0 dipole momenta are along the *z*-axis, and hence we give in the table only their *z*-component. \tilde{Q}^0 and $\tilde{\alpha}$ are respectively the unperturbed diagonal and degenerate molecular quadrupole and polarization matrices. The *q*'s are the atomic charges, d_{O-H} is the oxygen-hydrogen distance, HÔH is the molecular angle and *B*'s and *C*'s are the Buckingham parameters.

The Amoeba model [4] is an empirical potential for fully flexible water model which uses a polarizable atomic multipole description of the electrostatic interactions.



Fig. 1. Repulsive orientation not used in the parameterization: interaction energy (panel a) and molecular dipole variation ($\Delta\mu$) (panel b) vs the oxygen–oxygen distance R_{OO} . Solid line: CCSD(T) calculation; circles: SPW model.

The ASP-W4 model [5] uses an elaborate dispersion formulation and one-site polarizability up to guadrupole-guadrupole interaction. The recent reparameterization of the ASP potential based on the measured vibration-rotation-tunneling (VRT) data has lead to the VRT(ASP-W) model [6]. In this context, we proposed in a recent paper [7] a new simple water Hamiltonian, based on basic physical principles, which is defined by only four adjustable parameters similarly to the most commonly used SPC and TIP empirical models. In fact our model describes pair interactions and many-body effects in terms of atomic-molecular charge distribution, molecular polarizability and a simple semi-empirical potential only for short range atomic contacts. We use a charge density distribution which includes dipole and quadrupole effects, where all the corresponding atomic physical parameters involved in the Hamiltonian are obtained by first principles and direct evaluation of molecular observables, i.e. they are not adjustable parameters.

In this paper we present an optimization and a further application of our *simple polarizable water* (SPW) model to clusters [8,9] including 2 to 7 water molecules. Such clusters are of great importance in order to understand the physical and chemical properties of liquid water and ice as well as the hydration mechanisms of ions and molecules [10]. On the other hand, they are important benchmarks for testing our model, being considered as a bridge between the water molecule and the condensed phase.

2. Theory

2.1. The model

A detailed description of the SPW potential is given in our previous article [7], and here we just summarize the main features and limits of the model. There are three basic physical approximations of SPW.

Firstly, the rototranslational degrees of freedom of each molecule are considered as completely classical mechanical coordinates, while both electronic and intramolecular nuclear degrees of freedom (i.e. stretching and bending modes) are considered as quantum mechanical ones.



Fig. 2. Interaction energy components in the dimerization orientation: charge-charge (dotted line), polarization (straight line), dipole-dipole (dashed line), charge-dipole (long dashed line), Buckingham (dotted-dashed line).



Fig. 3. Specific heat capacities at constant volume vs the number of water molecules in the clusters (nmol). The straight line is the theoretical expectation while the points are the computed values; T=15 K, number of MC steps: 5×10^6 .

Secondly, for any given rototranslational phase space position of the molecules, the system is assumed to be confined in its vibroelectronic ground state, i.e. the lowest Hamiltonian eigenstate of the system where all molecules have fixed rototranslational coordinates and conjugated momenta.

Thirdly, the energy changes of the Hamiltonian ground state as a function of the rototranslational coordinates are considered fully determined by the electronic energy variations (i.e. we neglect vibrational energy changes) and do not alter the molecule geometry, that is the nuclear intramolecular positions are virtually fixed.

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

In the SPW model the intermolecular energy U'_1 , due to the unperturbed molecular charge distribution, is approximated expanding oxygen and hydrogen charge distributions up to quadrupoles, while the interaction energy shift U'_1 , due to the molecular polarizability, is approximated by expanding the variation of molecular charge distribution up to dipoles. Defining with μ and μ^0 the multidimensional vectors of the actual and unperturbed molecular dipoles, we have

$$\mu \cong \mu^0 + \widetilde{\Theta}\mu \tag{1}$$

where, if *n* is the total number of molecules, μ and μ^0 are 3n dimensional vectors and $\tilde{\theta}$ is a $3n \times 3n$ matrix which depends on the polarizability matrix α and on the positions of the molecular centers of mass [7]. Eq. (1) can be easily solved by inversion providing for each rototraslational configuration of the system, the molecular dipoles which can be used to obtain the energy term U'_{II} .

The previous approximations are clearly not valid at very short intermolecular distances, where higher order energy terms become relevant. In our model we treat such short range interactions using a semi-empirical energy term (Buckingham potential, \mathcal{U}_{SR}), which, in principle, includes all the energy terms disregarded in the expansions mentioned above. Note that we only consider short range repulsive interaction in the Buckingham potential as the short range attractive ones due to the induced dipole–induced dipole interaction are treated by the polarization term.



Fig. 4. Equilibrium structures of clusters.

The SPW potential $\mathcal{U}'(x)$ can be written as:

$$\mathcal{U}'(x) \cong \mathcal{U}^{0'} + \mathcal{U}'_{\mathrm{I}}(x) + \frac{\mathcal{U}'_{\mathrm{II}}(x)}{2} + \mathcal{U}'_{\mathrm{SR}}(x) \tag{2}$$

where

$$\begin{aligned} \mathcal{U}'_{1}(x) &= \sum_{i} \sum_{j>i} \sum_{l_{i}} \sum_{l_{j}} K_{el} \Bigg[\frac{q_{l_{i}}q_{l_{j}}}{|r_{N_{l_{j}}} - r_{N_{l_{i}}}|} + \frac{q_{l_{j}}\mu_{l_{i}}^{0} \cdot [r_{N_{l_{j}}} - r_{N_{l_{i}}}]}{|r_{N_{l_{j}}} - r_{N_{l_{i}}}|^{3}} - \frac{q_{l_{i}}\mu_{l_{j}}^{0} \cdot [r_{N_{l_{j}}} - r_{N_{l_{i}}}]}{|r_{N_{l_{j}}} - r_{N_{l_{i}}}|^{5}} \Bigg] \end{aligned}$$

$$(3)$$

$$\mathcal{U}'_{\mathrm{II}}(\mathbf{x}) = -\sum_{i} \left(\mu_{i} \cdot \sum_{j>i} E_{j} - \mu_{i}^{0} \cdot \sum_{j>i} E_{j}^{0} \right)$$
(4)

$$\mathcal{U}'_{SR}(x) = \sum_{i} \sum_{j>i} \sum_{l_i} \sum_{l_j} B_{l_j} B_{l_j} e^{-C_{l_i} C_{l_j} |r_{N_{l_j}} - r_{N_{l_i}}|}$$
(5)

where *i* and *j* refer to the molecules, l_i and l_j to the atoms of the molecules *i* and *j* respectively, $K_{el}=1/(4\pi\epsilon_0)$ and q_{ij} , μ_{lj}^0 , and r_{Nij} are the total charge, the unperturbed dipole (electric moment) and the position of the l_j atom. In Eq. (4) μ_i is obtained by the inversion of Eq. (1) and the expression of E_j and E_j^0 (the actual and the unperturbed electric field felt by the *i*-th molecule due to the *j*-th one) is given by the molecular dipoles [7]. 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 use repulsive interactions.

Finally, the SPW potential was better defined in this work by considering a minimum molecular center of mass-center of mass and oxygen-hydrogen distances (2.9 Å and 1.6 Å respectively) for intermolecular interactions, i.e. in our model at those distances an infinite energy barrier is present, implying that configurations at shorter distances are inaccessible. Such a feature of the SPW Hamiltonian is justified by the huge energy increase at short intermolecular distances and by the mixing electrons effects, occurring in very close molecular pairs, which cannot be described by a potential based on molecular properties as SPW.

It is worth to note that the hard-sphere atomic-molecular cores, although typically absent in the atomistic force fields used in molecular simulations, have been often utilized in statistical mechanical models of soft condensed matter based on atomic-molecular correlation functions [11–14]. In particular, Ninham et al. [15,16] extensively developed and applied a model for a water-like solvent based on the combined use of the molecular hard-sphere cores and

Table 2	
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Model	R _{OO}	θ_{a}	β
ab initio (a)	2.907	56.9	4.2
ab initio (b)	2.925	51.8	4.3
ASP-W4	2.970	57.0	-2.1
Amoeba	2.892	57.2	4.2
VRT(ASP-W)	2.952	48.5	2.3
MCDHO	2.916	56.1	3.8
TIP4P	2.750	46.0	1.2
SPC	2.750	52.0	22.0
SPW	2.880	68.2	8.1
Experimental	2.952	58.0±6.0	0.0 ± 6.0
	2.976	57.0±10.0	-1±10

The O–O distance is expressed in Å and the angles in degrees. The ab initio data (a) [25] are based on CCSD(T)/TZ2P(f.d)+dif corrected for BSSE. The ab initio data (b) [26] are evaluated at MP2/ANO level CCSD(T) corrected.

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Structural parameters of the dimer C_i

Model	α	β	ϕ	R _{OO}	R _{OH}
ab initio	112.3	68.0	142.4	2.776	2.266
ASP-W4	110.8	69.2	136.7	2.839	2.355
SPW	119.0	60.9	109.9	2.731	1.988

The O–O and O–H intermolecular distances are expressed in Å and the angles in degrees. The ab initio data were evaluated at MP2/6-311+G(d,p) level [22].

dipolar interactions. However, such a model, designed to be used in the framework of approximated correlation equations, was constructed on an extremely simplified molecular description (a nonpolarizable point dipole embedded into a hard-sphere), neglecting the atomic details of water–water interactions (e.g. hydrogen–hydrogen bonding) essential to properly model the liquid water behavior.

2.2. Definition of the second virial coefficient

The virial expansion [17] of the pressure leads to the definition of the virial coefficients.

$$P = \frac{NkT}{V} \left[1 + {\binom{N}{V}}B(T) + {\binom{N}{V}}^2 C(T) + \cdots \right]$$
(6)

At low density, the virial expansion can be truncated at the second term, given by B(T). This is a global property due to the intermolecular interactions assumed to be limited to single pair interactions.

B(T) can be written as a sum of a classical term [17]

$$B_{\rm cl}(T) = -\frac{1}{2} f\left(\langle e^{-\beta \mathcal{U}} \rangle_{\gamma} - 1 \right) dR \tag{7}$$

with the translational and rotational quantum corrections to order \hbar^2 [17].

$$B_{qn}^{tr}(T) = \frac{\hbar^2}{24(kT)^3} \int \frac{\langle |F^2| e^{-\beta \mathcal{U}} \rangle_{\gamma}}{M} dR$$
(8)

$$B_{qn}^{\text{rot}}(T) = \frac{\hbar^2}{24(kT)^3} \sum_{\alpha} \int \frac{\langle T_{\alpha}^2 e^{-\beta \mathcal{U}} \rangle_{\gamma}}{I_{\alpha}} dR$$
(9)

Here \mathcal{U} is the pair interaction energy, F the total force acting on one molecule, M the molecular mass, T_a the component of the molecular torque along the principal molecular reference frame axis α , I_{α} the corresponding moment of inertia, R the coordinates of the center of



Fig. 5. Second virial coefficient as a function of temperature.

Table 4

Structural parameters of the trimer

Model	θ	ϕ	ω	R _{OO}
ab initio [30]	1.9		46.3	2.782
VRT(ASP-W) [6]	0.6	31.6	57.3	2.800
FIRVRT [29]				2.850
Amoeba [4]				2.806
MCDHO [3]	1.0	33.1	65.0	2.911
TIP4P [18]	15.9	24.0	46.8	2.761
SPW	7.5	27.4	53.3	2.832
Experimental [31]	0.0			2.960
				2.845

The distances are expressed in Å and the angles in degrees. The ab initio data [30] are evaluated at the MP2/aug-cc-pVQZ level.

Table 6

Structural parameters of the cyclic pentamer

Model	θ	ω	au	R _{OO}	R _{OH}
ab initio (a)	6.0			2.867	1.913
ab initio (b)	1.0			2.697	
VRT (ASP-W) [6]	1.7	64.7	15.5	2.720	
FIRVRT [29]				2.750	
Amoeba [4]				2.756	
MCDHO [3]				2.753	1.766
TIP4P [18]	2.5	36.6	46.5	2.720	1.765
SPW	13.8	88.2	10.1	2.770	1.852
Experimental [34]				2.765	

The distances are expressed in Å and the angles in degrees. The ab initio data (a) [32] are evaluated at the HF/aug-cc-pVDZ level. The ab initio data (b) [34] are evaluated at the DZP+diff/Blyp level.

mass of the molecule, and $\langle \rangle_{\gamma}$ is the statistical average over the Euler angles γ (non-Boltzmann weighted).

3. Computational methods

In the present work we have re-evaluated, with higher accuracy, the Buckingham repulsive parameters, through a procedure identical to the one described in our previous paper [7]. The new, optimized Buckingham parameters are shown in Table 1, together with other physical properties defining our model.

As in our previous work [7], the agreement between the dimer interaction energy, evaluated by quantum chemical calculations, and the model prediction is very good also for those orientations which were not used in the parameterization (Fig. 1). The maximum errors never exceed 10^{-3} a.u. and the SPW model reproduces accurately the shapes of the curves.

In Fig. 2 the various components of the interaction energy in the dimerization orientation are shown. The relevant role of charge-charge and charge-dipole interaction is evident, while the polarization term represents about 5–10% of the total energy for separations below 3 Å.

Clusters of increasing dimension from two to seven water molecules were studied through Monte Carlo Metropolis (MC) canonical simulations. The starting structures were taken from the Cambridge Cluster Database and correspond to those global minima of the TIP4P [18] potential (as obtained from MC Basin Hopping minimization) which are supposed to be similar to the SPW global minima. The MC simulation procedure was set according to the literature [19,20]. The structural properties of clusters with minimal energy were obtained by simulations of 5×10^6 MC steps at 15 K. The convergence of the simulations was ascertained by comparison of the computed excess heat capacity (obtained by the potential energy fluctuations) with the corresponding expected harmonic value (Fig. 3).

Finally the virial coefficient was evaluated at seven different temperatures in the range 273.15–873.15 K. Since it only involves pair interactions, it was obtained through very long $(3 \times 10^7 \text{ steps})$ MC

Table J			
Structural	parameters	of the	tetramer

Table 5

Model	θ	ϕ	ω	R _{OO}	R _{OH}
ab initio [32]	0.4		67.6	2.743	1.758
VRT(ASP-W) [6]	0.4	12.3	67.6	2.740	
FIRVRT [29]				2.780	
Amoeba [4]				2.760	
MCDHO [3]	0.1		67.1	2.806	1.842
TIP4P [18]	6.1	2.9	41.1	2.723	1.774
SPW	3.7	14.5	51.2	2.787	1.855
Experimental [4,33]				2.790	
				2.845	

The distances are expressed in Å and the angles in degrees. The ab initio data [32] are evaluated at the MP2/aug-cc-pVDZ level.

simulations of a water dimer system with one molecule fixed in the center of the box and the other free to move all around through the MC steps. The maximum distance (14 Å) between the two molecules was evaluated with an accurate sensitivity analysis, showing that the inclusion of configurations at an intermolecular distance beyond 14 Å did not significantly modify the virial coefficient. The quantum translational and rotational contributions to the virial coefficient, requiring the evaluation of the interaction forces, were obtained by numerical derivation of the potential.

4. Results and discussion

As mentioned in the previous section, we have tested the good convergence of the MC simulations by comparing the excess heat capacities for the clusters, obtained by the potential energy fluctuations at 15 K, with the expected harmonic values. From the excellent agreement of MC results with the corresponding harmonic values, shown in Fig. 3, a high convergence of the simulations can be inferred.

The water dimer (Fig. 4) is the most widely studied cluster both theoretically and experimentally. Its PES has been investigated in great details by quantum ab initio calculations suggesting the existence of ten local minima of different geometries [21,5,22].

In this work we analyze the global minimum geometry which exhibits a C_s symmetry [21,23,24] with a single hydrogen bond in trans configuration, and a cyclical local minimum of C_i symmetry [24]. In the latter the free hydrogen atoms alternate above and below the O–H–O–H plane. The relevant structural parameters of both C_s and C_i minima, as provided by models of different complexity [25,26,18,3–6,1] and by experimental data [3,4], are reported in Tables 2 and 3. Interestingly, Table 2 shows that models based on complex Hamiltonians (i.e. making use of a large number of adjustable parameters) and quantum ab initio calculations do not perform much better than simple models, when compared to experimental data. The SPW model is only slightly worse than quantum ab initio calculations and the more sophisticated models, being in general better than SPC and TIP4P based on empirical Hamiltonians with a complexity similar to the SPW.

Table 7 Distanc

Distances Roo an	d <i>R</i> _{он} , i	in Å, ener	gy in kc	al/mol for	the hexame	cage and	prism
00	011/		0.5				F

Model	Cage			Prism	Prism		
	R _{OO}	R _{OH}	Е	R _{OO}	R _{OH}	Е	
ab initio (a)	2.807	1.876	-44.04	2.840	1.956	-43.97	
ab initio (b)	2.828	1.896	-46.48	2.861	1.975	-46.41	
Amoeba [4]	2.797		-45.89	2.844		-41.78	
MCDHO [3]	2.888	1.944	-43.73	2.892	2.001	-44.23	
TIP4P [18]	2.757	1.829	-47.31				
SPW	2.846	1.923	-49.03	2.881	1.983	-49.99	

The ab initio data [35] are evaluated: (a) at the MP2/TZ2P++ level and (b) at B3LYP/TZ2P(f)++ level. The (b) energies are obtained from B3LYP/6-311++ G^{**} calculation as in Ref. [36].

Table 8

Distances R_{OO} and R_{OH} , in Å, for the heptamer

R _{OO}
2.807
2.814
2.762
2.846

The ab initio data [37] are evaluated: (a) at the MP2/IZ2P++ level and (b) at B3LYP/6-311++C** level.

In order to evaluate the reliability of the SPW, we have also investigated its accuracy in reproducing the second virial coefficient of water. In Fig. 5 we compare the quantum corrected values of the virial coefficient, as obtained by the SPW Hamiltonian, with experimental data [4] and other theoretical/computational results based on molecular potentials of different complexity [18,3-5,27,28]. It is essential for a reliable water potential to be able to reproduce the second virial coefficient, which is an indirect measure of the accuracy of the dimer PES. From the figure, it is evident that the SPW model reproduces reasonably well the experimental results, even though no virial data have been used in the SPW parameterization. Note that both ASP-W4 and MCDHO models (showing a higher accuracy) involve many adjustable parameters (about 70 for ASP-W4 and 20 for MCDHO). On the other hand, our results are again better than SPC and TIP4P ones, with a significant improvement at low temperature. It must be noted that the large SPW quantum contribution, essentially provided by the rotational term, is due to the small moments of inertia of the water molecule.

Structural analysis of the other water clusters is shown in Tables 4–8. The structures of the clusters with minimum energy obtained with the SPW model are shown in Fig. 4. The tables clearly indicate that the SPW model is significantly closer to quantum ab initio calculations than TIP4P, providing structural parameters of intermediate accuracy at the energy minima. Interestingly, in the hexamer, the smallest water cluster with really 3-dimensional (non-planar) structures, the SPW model provides a prism energy which is about 1 kcal/mol lower than the cage one. This result is in excellent agreement with experimental and theoretical findings [38–40] showing that the prism should correspond to the global energy minimum when neglecting the vibrational zero point energy.

It must also be noted that SPW Hamiltonian reproduces quite well the expected exponential decrease in the oxygen–oxygen distance, R_{OO} , as a function of the cluster size for cyclic clusters, converging to the value of the common Ih ice [41,42,32].



Fig. 6. Energy minima per molecule (kcal/(mol)) vs cluster size(nmol).



Fig. 7. Relative polarizability interaction weight vs cluster size(nmol).

Finally in Fig. 6 we compare the SPW energy per molecule of the cluster structures with the corresponding values obtained via quantum ab initio (MP2) and DFT (BLYP) [36] calculations and empirical or semi-empirical models [18,3,4,43,44]. From this figure it is evident that SPW model provides a very accurate description of the energy as a function of the cluster size for all the clusters studied, resulting as one of the best model in reproducing quantum ab initio calculations.

It is interesting to note (see Fig. 7) that, in the SPW model, the polarization interaction term provides typically about 10% of the overall cluster interaction energy with the dimer corresponding to highest polarization energy (20%), in very good agreement with previous results [45] and the pentamer corresponding to the lowest (less than 5%).

5. Conclusions

In this article we have shown that a relatively simple water model (SPW), based on physical first principles and involving a very limited number of adjustable parameters, can be used to describe rather accurately the essential physics of water clusters ranging from dimer to the heptamer. In such a model, only short range atomic repulsion is described by a semi-empirical energy function involving only four parameters.

The results obtained show that the SPW model, despite its simplicity, provides an intermediate accuracy between simple empirical models (SPC and TIP4P) and the most sophisticated water models based on a large number of adjustable parameters (MCDHO, Amoeba, ASP). We believe that SPW model might be efficient and reliable for simulating water molecules regardless of their specific temperature/density state; in particular it may turn to be very useful for studying the thermodynamics and kinetics of chemical reactions in water clusters, where the polarization contribution can be relevant and the reactants can be treated with quantum calculations at electronic level (e.g. Perturbed Matrix Method [46–48]).

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