

Ab initio based polarizable force field parametrization

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Experimental and simulation studies of anion-water systems have pointed out the importance of molecular polarization for many phenomena ranging from hydrogen-bond dynamics to water interfaces structure. The study of such systems at molecular level is usually made with classical molecular dynamics simulations. Structural and dynamical features are deeply influenced by molecular and ionic polarizability, which parametrization in classical force field has been an object of long-standing efforts. Although when classical models are compared to *ab initio* calculations at condensed phase, it is found that the water dipole moments are underestimated by $\sim 30\%$, while the anion shows an overpolarization at short distances. A model for chloride-water polarizable interaction is parametrized here, making use of Car–Parrinello simulations at condensed phase. The results hint to an innovative approach in polarizable force fields development, based on *ab initio* simulations, which do not suffer for the mentioned drawbacks. The method is general and can be applied to the modeling of different systems ranging from biomolecular to solid state simulations.
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The study of halide anions in water solutions has recently gained a renewed interest both in theoretical and experimental studies. Understanding the molecular level detail of anion-water interaction is of fundamental importance to explain (i) the behavior of water interfaces (that affect biological, atmospheric, pharmaceutical, and industrial processes),^{1–4} (ii) the dynamics of solvation shell in the bulk (which can now be probed with ultrafast spectroscopic techniques),^{5–11} and (iii) the mechanism for nanobubbles' coalescence (salts show the tendency to slow it down).^{12,13} It is now accepted that all the above mentioned phenomena are strongly affected by the molecular polarization that plays a fundamental role in determining the structural, orientational, dynamical, and thermodynamical properties of the system. Accounting for nonadditive forces in liquid water allows one to accurately predict the relative contribution of hydrogen-bond interactions and gives a reasonable description of water-liquid interface.^{14,15} Also, the ionic surface propensity is substantially due to ion and water polarizabilities; in fact, given their high polarizability, anions tend to be extremely polarized mainly in asymmetric solvation environments such as small clusters and surfaces (where incomplete solvation shell induces a sizable dipole on the anion). In this case, a good description of ion polarization is of uttermost importance.³ The ideal way of studying such systems would be the recourse to *ab initio* molecular dynamics (MD) simulations.¹⁶ Unfortunately, it still constitutes a huge computational effort to obtain quantitative results and good statistics for “big” systems. Force field simulations still represent the main theoretical technique to study problems, such as, for example, interfaces and concentrated solutions. Even though a huge effort has been dedicated during the past

20 years in the implementation of refined classical force fields, the inclusion of molecular polarization is still far from being a closed issue. New and sophisticated polarizable force fields are required to provide more quantitative and converged results, as recently highlighted by the *Journal of Chemical Theory and Computation* in a special issue on polarization.¹⁷ One of the largest limitations of standard molecular-mechanics (MM) polarizable force fields was remarked few years ago by Kaminski *et al.*¹⁸ and by Giese and York.¹⁹ They found that the transferability of gas phase derived potentials to condensed phase is hindered by the absence of polarization exchange coupling in classical models. This effect was shown on bifurcated water chains (BWCs), where strong intermolecular interactions amplify the nonadditive induction effects. Nevertheless, Piquemal *et al.*²⁰ showed that both the *ab initio* polarization energy and dipole moments of bifurcated water oligomers of various size (including BWC) could be easily reproduced if the anisotropic polarizability of the water molecule is fairly described. A similar result was independently reached by the author and co-workers for a different system (a “simple” ion-water dimer).^{21,22} It was also found^{23,24} that the problem of explicitly treating *Pauli effects*²⁵ in the multibody interaction can be solved with the introduction of an *intermolecular* damping function (similar to the *intramolecular* ones introduced by Thole²⁶). The use of damping functions together with the point dipole (PD) method²⁷ represents an ideal tool to model the polarizable ion-water system in MD simulations.^{23,24} Its validity was demonstrated for dimers at gas phase; the induced dipole moment, which is computed as a function of the ion-water distance for five different orientations of the dimers, could reproduce with the results of *ab initio* CCSD(T)/aug-cc-pVTZ calculations high accuracy. Piquemal *et al.*²⁸ and Jiao *et al.*²⁹ further extended this approach to

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include energetic criteria based on the *ab initio* polarization energy. It was suggested that such model would be a good candidate to reliably reproduce the polarizable interaction both in gas phase and in bulk. Indeed, it has been already used in liquid phase simulations.^{28,29} Nevertheless, the true effectiveness of these models, as compared to the existing ones, has never been demonstrated. Moreover, although the proven sensibility of anion-water systems on polarization, the author is not aware of any rigorous tests for the treatment of the polarizable interaction which is required in order to assess quantitative properties of the anion-water interaction in condensed phase. Even if the use of such approximations has given structural results in fair agreement with the *ab initio* results, other properties are badly reproduced such as, for example, the total dipole moment of water which is underestimated by $\sim 30\%$ (Refs. 30 and 31) (considered that polarizable models are used to compute the *induced* dipole moment, one should be aware that the error in this quantity is almost 50%!).

The approach proposed here is based on the results of Car–Parrinello MD (Ref. 32) simulations of a chloride ion with 64 water molecules. The temperature and density of the system were set to ambient conditions. Troullier–Martins pseudopotentials³³ with a 70 Ry cutoff together with the the BLYP functional^{34,35} were used. The time step was set to 4 a.u. and the fictitious mass for the orbital was chosen to be 400 amu. Periodic boundary conditions were applied. After having equilibrated the system for 10 ps, a production run of 30 ps was made. For each configuration, water and chloride dipole moments of the *ab initio* calculation were computed using the ions' and Wannier centers^{36–38} coordinates. Within this approach, Q_i being the core charge of the i th nucleus at position $\vec{R}_i(t)$, $q_j = -2e$ as the charge of closed-shell Wannier orbitals holding two electrons with centers at $\vec{r}_j(t)$, and N_I and n_I as the number of ions and Wannier centers that are assigned to the I th molecule, the dipole moment of a molecule I is given by

$$\vec{\mu}_I = \sum_{i=1}^{N_I} Q_i \vec{R}_i + \sum_{j=1}^{n_I} q_j \vec{r}_j. \quad (1)$$

By definition, $\vec{\mu}_I$ will be independent of the coordinate frame of reference only if the molecular fragment is neutral. If the molecule is charged, the dipole moment must depend on the origin of the coordinate system. Since we deal both with charged and neutral species, which move in space, the most natural frame of reference for computing dipole moments is the molecular center of mass. For the same configurations, the molecular dipole moments were calculated by using the PD2-H2O classical model introduced in Ref. 21. This model contains a dummy site M lying at a distance of 0.06 Å from the oxygen on the permanent dipole moment versor. Within our approach, charge-charge and charge-dipole interactions are screened by Gaussian damping functions^{23,24} given, respectively, by

$$f_{q-q}(r) = \operatorname{erf}\left(\frac{r}{a}\right) - \frac{2}{\sqrt{\pi}} \left(\frac{r}{a}\right) e^{-r^2/a^2}, \quad (2)$$

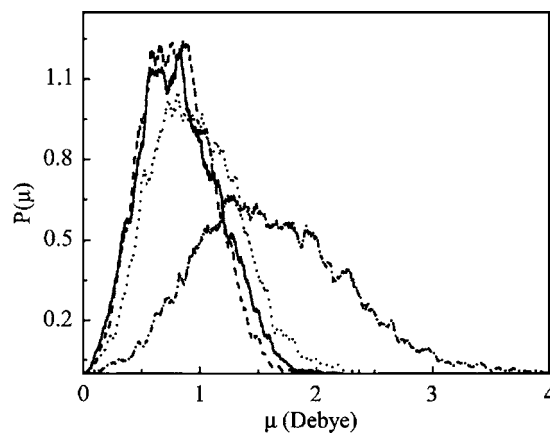


FIG. 1. $P(\mu)$ for the chloride ion. Comparison between *ab initio* results (solid line), PD2-H2O with damping (dashed line) and without damping (dash-dotted line) and with the anion polarizability lower than its gas phase values (dotted line, $\alpha_{\text{Cl}} = 4 \text{ \AA}^3$).

$$f_{q-\mu}(r) = \operatorname{erf}\left(\frac{r}{b}\right) - \frac{2}{\sqrt{\pi}} \left(\frac{r}{b}\right) e^{-r^2/b^2} \left[1 + \frac{2}{3} \left(\frac{r}{b}\right)^2 \right], \quad (3)$$

where the parameters $a_{\text{ion-M}} = 0.00$, $b_{\text{ion-M}} = 7.64$, $a_{\text{ion-H}} = 1.51$, and $b_{\text{ion-H}} = 0.00$ are given by the average of the values a_i^{opt} and b_i^{opt} optimized at each time step; they were obtained by applying the simplex algorithm to minimize the penalty function $\chi = \sum_{i=1}^N (|\vec{\mu}_i^{\text{Cl}}| - |\vec{\mu}_i^{\text{AI}}|)^2$, where N is the number of molecules and the superscripts Cl and AI stand for classical and *ab initio* computed values, respectively. In the case of $\text{O} \cdots \text{O}$ and $\text{O} \cdots \text{H}$ intermolecular interactions, no damping terms were used. The anion polarizability was set to its gas phase value³⁹ ($\alpha_{\text{Cl}} = 5.4822 \text{ \AA}^3$). All the interactions were computed within the minimum image convention using a cutoff radius equal to half of the simulation box size.

The dipole moment distribution function $P(\mu)$ of the anion and of water were computed in order to compare the results obtained to the *ab initio* simulations and classical ones. This criterium is similar to the one previously used for studying the electrostatic properties of dimers at gas phase.^{21–24} An approach based on energetic properties as the one proposed in some recent studies^{28,29} for gas phase systems could not be applied here because a partitioning of the *ab initio* energy in different contributions (polarization, van der Waals, etc.) was not feasible for the liquid state considered.

The chloride $P(\mu)$ (see Fig. 1) reveals basic features of three different classical models. If the anisotropic model developed for water in Ref. 21 is used without any damping functions, the anion dipole moment is terribly overestimated; not only it peaks where the *ab initio* $P(\mu)$ is decaying fast to zero but it also shows a long tail up to ≈ 4 D. Such huge overpolarization of the anion is due to those configurations where water lies close to it,²⁴ in fact, in all PD models, the induced dipole moment tends to diverge when two molecules are near. This effect was already known in the case of intramolecular polarization as the *polarization catastrophe*,²⁶ which due to neglecting of electron density overlapping at short distances, causes the induced dipole moment to diverge to infinity. To face this problem, most of the approaches used

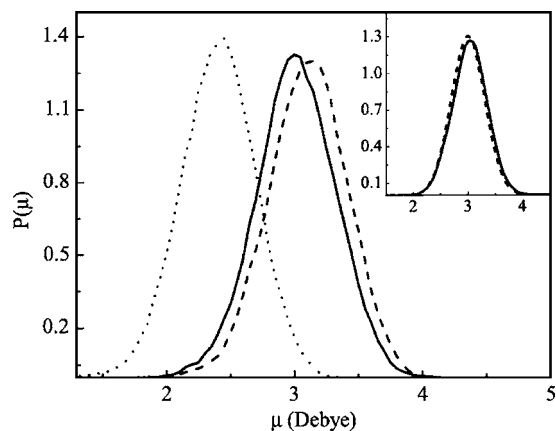


FIG. 2. $P(\mu)$ of water molecules in the chloride first solvation shell and of bulk water molecules (inset). Comparison between *ab initio* results (solid line), PD2-H2O (dashed line) and PDM-H2O (dotted line) models.

up to now in classical simulations are based in assigning a low polarizability to the anion;^{11,40,41} it will be shown below that, although this remedy allows to prevent the polarization catastrophe (basically by underestimating the induced dipole moment), it does not hinder the divergence at short distance. The results obtained using a low value for chloride polarizability are shown in Fig. 1. It is evident that the curve is much closer to the *ab initio* one, but it has still a tail which accounts for an overpolarization of $\approx 25\%$. Moreover, this distribution is broader and the peak is lower and slightly shifted to high values of the dipole moment. Given these results, one could be tempted to further reduce the chloride polarizability until a good agreement is reached. Even though it would be an easy way out of the problem, it would not guarantee that all the other properties (first of all the structural ones) are fairly reproduced. On the other hand, it could be appreciated that the use of a fine tuned damping function allows to reproduce the *ab initio* $P(\mu)$ with highest precision (see the comparison of heights, widths, and tails of *ab initio* and classical damped models in Fig. 1); furthermore, the use of this parametrization allows for force field transferability, being the same model that is good also for dimers at gas phase. In systems where heterogeneous environments induce a high dipole moment on the chloride, the divergence at short distance would influence even more the differences in the distributions obtained with the damped and the no-damped models. For example, given that the surface propensity of the chloride ion (and of the bigger halogenide anions) is explained as a minimum in the free energy at the surface due to ion polarization,³ an exact modeling of polarizable interactions would provide more accurate quantitative estimates of the phenomenon. In the Introduction, it was pointed out that the solvent polarization also plays an important role; nevertheless, in some recent studies,^{30,31} it was found that water molecules are underpolarized as compared to Car–Parrinello simulations. This is clearly shown in Fig. 2, where the performance of the PDM-H2O and PD2-H2O models with optimized damping parameters^{21–24} is compared. In Fig. 2, the $P(\mu)$ of water molecules in the first solvation shell of the anion is shown; these molecules sustain the highest perturbation in the dipole moment distribution

due to the strong interaction with the anionic charge and dipole moment. The PDM-H2O is a simple isotropic model which is able to reproduce with a small error the electrostatic properties of chloride-water dimers.²⁴ Nevertheless, as for other models used in the previous studies,^{30,31} when it is transferred to condensed phase, it does not perform so well since the water dipole moment is underestimated by $\sim 25\%$. On the other hand, the PD2-H2O model performs fairly well, showing a small shift of ~ 0.2 D with respect to the *ab initio* curve. Bulk water molecules do not seem to feel the polarizing effect of the ion, their average dipole moment being the same as in the previous calculations⁴² of pure liquid water. In the inset it can be appreciated that the $P(\mu)$ obtained with the PD2-H2O model for bulk water is almost superposable to the *ab initio* curve.

The above results prove that by using a simple anisotropic polarizable model as the one presented here, one is able to extremely improve the agreement between classical and *ab initio* simulations without any noticeable added computational cost; in fact, the PD algorithm is the same as that used in previous (less precise) classical simulations and the calculation of the damping functions does not imply important overheads. The implementation of this model in actual MD simulations will be the topic of a forthcoming contribution.

Finally, what is discussed up to this point suggests some speculations about polarizable force field parametrization. In a recent application of the force-matching algorithm^{43–46} for parametrizing biomolecular force fields from QM/MM simulations, Maurer *et al.*⁴⁷ pointed out that to get an improved agreement of QM/MM results with classical simulations, the implementation of the next generation force fields for condensed phase simulations will require the abandoning of the fixed point-charge description with optimized parameters for an explicit polarizable parametrization. The method used here indicate how such a step forward could be taken within *ab initio* MD simulation schemes (either Car–Parrinello or Born–Oppenheimer): the second moments of the electrostatic interaction can be parametrized by a fitting of the dipole moments distribution as obtained by the coordinates of the Wannier centers and of the ions along the dynamics [see Eq. (1)]. Since it is not needed to calculate the Wannier centers position at each time step, it is expected that the additional computational costs would be negligible compared to the cost of the whole calculation. On the other hand though, as shown here for the case of chloride in water, a remarkable improvement in the accuracy of the resulting force field would be gained. In fact, once the dipolar interactions are faithfully reproduced, there is no need to include their effects implicitly⁴⁸ in the remaining terms which model the dispersion interactions; consequently, considering that polarization often accounts for $\approx 20\%$ of the interaction energy,²⁵ also all the inter- and intramolecular force field parameters will be parametrized with better accuracy. The implementation of such an approach is straightforward in force-matching algorithm; nevertheless, it can be also coupled to any other technique for force field parametrization. Moreover, the method is independent of the functional form of the force field itself, in fact, any sophisticated polarizable model could be param-

etrized. Here, a simple three point polarizabilities anisotropic damped PD model was shown to be successful in reproducing the dipole moment of the chloride and solvent molecules. The general validity of this approach makes it a powerful instrument for the production of next generation force fields for any kind of systems.

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