

Modeling the ion-water interactions from first-principle calculations

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Synopsis Ion specific effects in aqueous environments are of fundamental interest in physical, chemical, and biological, as well as industrial systems, with a research topic focused on the modeling of ion-pair/ion-water/water-water interactions. So far, the water-water interactions has been widely studied what has lead to a variety of water potential models of increasing complexity. Although extensive experimental and theoretical studies have been reported, questions on how ions change the water network and the properties of their aqueous solutions are still open, demanding an accurate description of the underlying intermolecular forces. Thus, first-principles approaches are employed to develop generalized representations for these interactions coupled to available reliable water models for studying ion-hydrates from finite-size clusters to bulk solutions.

In the past years, experimental and theoretical efforts have been devoted to develop semiempirical ion-water force-fields for molecular dynamics applications, while more recently first-principles approaches have been developed to provide insights into the nature of such interactions. However, investigations are still constrained by the limited predictive abilities of the empirical models, the high computational cost for correlated *ab initio* methods, and the intrinsic deficiencies of common functionals in describing weak interactions. A fully *ab initio* approach to these appears, at first glance, daunting. However, progress has been made, with the most advanced *ab initio*-based approaches clearly being a step forward combining computational efficiency with fitting accuracy.

Thus, we adopted a bottom-up approach starting from small to medium size clusters, where valuable information has been acquired by IR experimental studies and *ab initio* computations. We focus on the representation of the interactions based on first-principle data of solvated monovalent (halide $X = F^-$, Cl^- , Br^- , I^-) and (alkali-metal $M = Li^+$, Na^+ , K^+ , Rb^+ , Cs^+) ions [1]. The new ion-water potential energy surfaces (PESs) are constructed by an extended version of the Thole type model (TTM) to describe halide/alkali-metal ion-water interactions in conjunction with different TTM-based water model potentials. The potential form is given by: $V_{tot} = V_{w_n}^{inter} + V_w^{intra} + V_{i-TTM}^{inter}$, where $V_{w_n}^{inter}$ corresponds to MB-pol, TTM4, TTM3 and TTM2 water models, and V_w^{intra} the PS water monomer PES. The new $V_{i-TTM}^{inter} = V_{TTM,elec} + V_{TTM,ind} + \sum_{i=1}^n (V_{rep}(R_{X/M,i}) + V_{disp}(R_{X/M,i}))$ PESs count with four contributions: electrostatic, induction, repulsion and dispersion interaction energy terms, with n being the number of surrounding water molecules. Thus, the potential functions explicitly count with polarization terms, include angular anisotropy in short- and long-range terms by adjusting to explicitly correlated CCSD(T)-F12 *ab initio* energies for mono-hydrates,

and CCSD(T) calculations for anion/cation polarizabilities, while dispersion coefficients are obtained from DFT/LC- ω PBE/aug-cc-pVTZ calculations using the XDM model (see Figure 1). By construction, these PESs are transferable to larger ion-water systems and bulk solutions. Therefore, the quality of the new generalized V_{tot} PESs and their performance are checked by comparing to computationally expensive *ab initio* CCSD(T)-F12/DF-MP2 calculations for larger ion-water (with n up to 8) systems, and compared to different DFT approaches assessing in a systematic way the performance of various functionals with and without dispersion corrections. [2, 3]

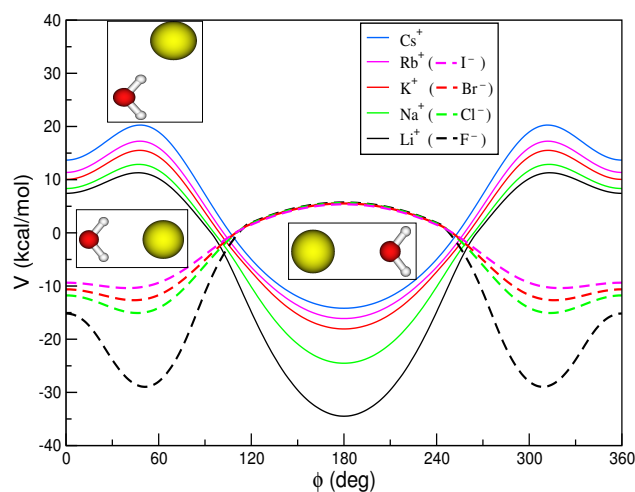


Figure 1. Minimum energy curves for $M^+(H_2O)$ (solid lines) and $X^-(H_2O)$ (dashed lines) potentials for planar configurations (specific structures are shown in the insets) along the azimuthal ϕ angle with H_2O molecule fixed at its vibrationally average geometry.

References

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