Exploring ion microhydration through quantum simulations: a bottom-up approach from nanoscale clusters to bulk solutions

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Dissolved ions in aqueous media are ubiquitous in many physicochemical processes, playing a crucial role in the structure of the water molecules network. A thorough understanding of the underlying forces from small finite-size clusters to bulk solutions is still challenging, motivating further investigations.

Thus, we introduced a systematic analysis of the interaction energies obtained from high-level electronic structure methodologies, to assess various dispersion-corrected density functional approaches, as well as *ab initio*-based data-driven potential models for halide ionwater clusters [1]. Following a bottom-up data-driven potential approach (see Figure 1), we have then looked into both classical and quantum behavior of poly-hydrated halides, employing an evolutionary programming procedure and classical/ quantum path-integral molecular dynamics simulations [1, 2].

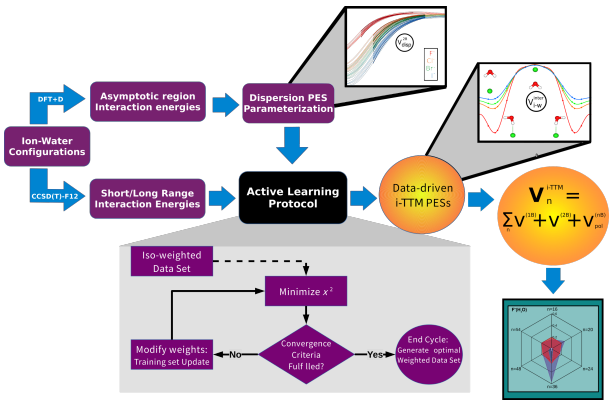

Figure 1: *Flowchart of the i-TTM potential models.*

Our data reveal that at low finite temperatures, nuclear quantum effects affect certain structural properties, such as weakening hydrogen bonding between the halide anion and water molecules, with minor distortions in the water network beyond the first hydration shell, indicating local structure rearrangements. Such structural characteristics and the promising cluster size trends observed in the single-ion solvation energies (see Figure 2) motivated us to draw connections of small size cluster data to the limits of continuum bulk values, toward the investigation of the challenging computational modeling of bulk single ion hydration.

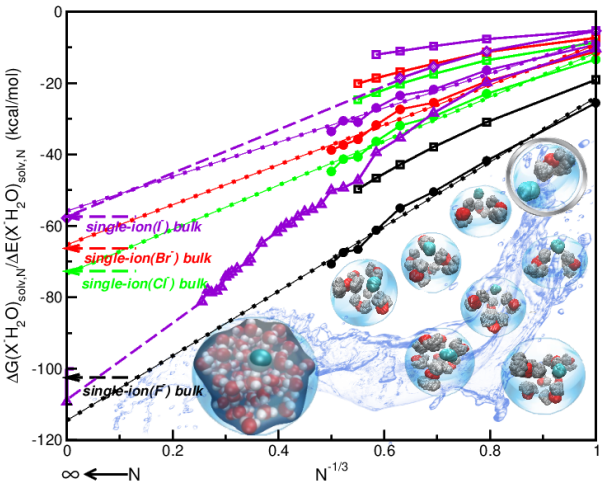

Figure 2: *Single-ion solvation energies as a function of clusters size.*

Index Terms: electronic structure calculations, benchmark datasets, data-driven modelling, ion hydration, quantum computer simulations

[1] Rodríguez-Segundo, R., Arismendi-Arrieta, D.J., and Prosmiti, R. "A Benchmark Protocol for DFT approaches and Data-Driven Models for Halide-Water Clusters", Moleculess 27:1654-1-16, 2022.

[2] Rodríguez-Segundo, R., Gijón, A., and Prosmiti, R. "Quantum molecular simulations of microhydrated halogen anions", Phys. Chem. Chem. Phys. 24:14964–14974, 2022.