Aqueous solvation of divalent cations and acids through Born-Oppenheimer molecular dynamics simulations and polarizable force fields

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Molecular Dynamics (MD) is nowadays a well established technique for the study of many systems of interest. However, the design (and parametrization) of force fields is still a difficult task. In particular the design of force fields to study the aqueous solvation of ions has been very challenging. An alternative approach is Born-Oppenheimer Molecular Dynamics (BOMD) where the forces between atoms are calculated “on the fly” from quantum calculations as the trajectory is generated. In this way the design of force fields is avoided and the task of force field design is instead finding the “right” approximation to solve the many-body Scrödinger equation.

In this talk we present the main results of our a studies of the microhydration properties of the cations Ca^{2+}, Mg^{2+} [1], and Pb^{2+} [2] applying the BOMD technique, the advantages and drawbacks of this methodology are discussed. The results are compared with experimental measurements of liquid structure (EXAFS spectra) and gas-phase infrared vibrational spectra. On the other hand, we present findings of the hydration features of arsenous, arsenic and hydrochloric acids, and the proton dynamics that occurs in these solutions [3]. Finally advances in the development of polarizable force fields for the correct simulation (and modeling) of asymmetric hemidirected cation hydration is presented.

[1] Aqueous solvation of Mg(II) and Ca(II): A Born-Oppenheimer molecular dynamics study of microhydrated gas phase clusters; C. I. León-Pimentel, J. I. Amaro-Estrada, J. Hernández-Cobos, H. Saint-Martin and A. Ramírez-Solís; J. Chem. Phys. 2018, 148, 144307.
[2] Born-Oppenheimer molecular dynamics studies of Pb(II) micro hydrated gas phase clusters; C. I. León-Pimentel, J. I. Amaro-Estrada, H. Saint-Martin and A. Ramírez-Solís; J. Chem. Phys. 2017, 146, 084307.
[3] On the aqueous solvation of AsO(OH)3*vs.* As(OH)3. Born–Oppenheimer molecular dynamics density functional theory cluster studies; A. Ramírez-Solís, J. I. Amaro-Estrada, C. I. León-Pimentel, J. Hernández-Cobos, S. E. Garrido-Hoyos and H. Saint-Martin; *Phys. Chem. Chem. Phys.*, 2018,20, 16568.