Fully Quantum Dynamics of Proton Transfer in water and aqueous solutions : the case study of the Zundel ion

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In this project, we develop and implement a new method which combines accurate Quantum Monte Carlo (QMC) calculations of the electronic contributions, with a Path Integral Langevin Dynamics (PILD) approach for the ionic part, in order to take into account thermal and quantum effects affecting the dynamics of hydrogen in water. While the QMC framework based on a many-body wavefunction, guarantees the necessary accuracy to describe the dispersive intermolecular forces, the PILD is able to provide a fully quantum treatment of protons by efficiently dealing with the intrinsic noise present in the QMC forces. The combination of the two approaches, i.e. QMC and PILD, represents an original and powerful tool to overcome the numerical and theoretical bottlenecks of proton dynamics simulations in water and aqueous systems. The first test case tackled in this project is the hydrogenated water dimer (Zundel ion), whose energy surface has been accurately resolved at the QMC level of theory [1]. Moreover, this system represents an ideal benchmark for our new method since it has been widely studied both theoretically and experimentally in the last fifty years. We have confirmed that, in this system, quantum nuclear effects (NQE) are important even at room temperature. The natural extension of this project is to apply our method to larger model ions and water clusters and to study the proton transfer in water and aqueous systems.

[1] M. Dagrada, Michele Casula, Antonino M. Saitta, Sandro Sorella & Francesco Mauri, Quantum Monte Carlo Study of the Protonated Water Dimer. *J. Chem. Theory Comp.* **10**,1980 (2014)