

Theoretical Spectroscopy: Full quantum dynamical study of the vibrational structure of hydrated hydroxide

D. Peláez

Laboratoire PhLAM, UFR Physique, Université de Lille 1, Villeneuve d'Ascq, France

In many processes, the impact of nuclear quantum phenomena cannot be neglected if a physically correct simulation is aimed for [1]. This quantum description of the nuclear motion is usually obtained by mapping the system onto a grid, thus implying a discretisation of the configuration space. As a consequence, all quantities take the form of high-order tensors. Unfortunately, multidimensional representations imply an exponential scaling of data and the concomitant number of operations with system size as well as the difficulty of computing multidimensional integrals [2].

Solutions to these issues, in particular when considering the representation of the potential energy surface, exist in the form of tensor-decomposition schemes. We present the recently developed the Multigrid POTFIT (MGPF) algorithm [3] which alleviates the exponential scaling by avoiding the calculations on the full grid. Moreover, we introduce our latest improvements to the algorithm which provide numerical stability and higher accuracy through the use of non-product grids for combined modes [4].

We illustrate the power of the MGPF algorithm in conjunction with the Multiconfiguration Time-Dependent Hartree (MCTDH) method in the case of the full-dimensional (9D) study of the vibrational structure [5] and the computation of the infrared spectrum [6] of the hydrated hydroxide complex (H_3O_2^-).

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