Mathematical Methods for Ab initio Quantum Chemistry

Workshop

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Flexible Potential Energy Surface from Iterative Calculations of Rovibrational Molecular States

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The quest to accurately describe the condensed phases of water has precipited the developement of a enormous potential energy surface (PES) for water's clusters. All these PES consider the pairwise additive approximation which consist on developping the N body potential energy function as a sum of two body potentials. Despite the large number of ab initio PES, never of them is able to accurately reproduce the experimental transitions observed in microwave and far infra-red region for the water dimer. The principal limitation of these PES arise from the fact that each monomer of the dimer was considered as rigid and do not consider the deformation of intramolecular coordinates $\{\mathbf{q}\}$. In this talk, I will present an adiabatic scheme used to include a flexibility in a rigid PES for the water dimer. This adiabatic decoupling between the intramolecular $\{\mathbf{q}\}$ and the intermolecular coordinates $\{\mathbf{Q}\}$ of the water dimer, is equivalent of the Born Oppenheimer approximation currently involved in electronic calculations. Fitting of the flexiblle PES to the IR transitions was effectued by an heuristic optimization scheme coupled to the non linear Levenberg Marquart algorithm. This minimization step required the calculation of rovibrational eigenstates of the water dimer which were obtained from a a pseudo spectral scheme coupled to the Lanczos algorithm. This iterative method was shown to be very efficient because it only requires the application of the hamiltonian operator on a seed vector

$$|u_{n+1}\rangle \propto \left\{\hat{\mathbf{H}} - \alpha_n\right\} |u_n\rangle$$

and not the matrix representation $\mathbf{H}$. The new flexible PES obtained from this fit gives a very good agreement with spectroscopics and thermodynamics data available.