Path Integral Methods for Isotopic Fractionation of Li and Proton Diffusion in Hydroxides

Romain Dupuis, MIT (Boston)

The Path Integral Molecular Dynamics method has become a reference for computing Quantum Nuclear Effects. In this presentation, we address two modern scientific questions using key developments such as high order estimators[1], Thermodynamics Integration coupled with PIMD (TI-PIMD)[1, 2] and real-time dynamics[3].

Firstly, we investigated the isotopic fractionation of lithium which is used as a geological marker. It is a quantum property that could be used as a test case for quantum methods.The TI-PIMD prevails over other methods because it treats anharmonicity and gives a direct access to the free energy. To obtain good statistics, it was necessary to enhance the sampling of the trajectory, which was done developing the virial 4 th order estimator[1]. Besides, the coupling of PIMD with thermodynamics integration was improved[1, 2]. The calculated isotopic fractionation is in agreement with experimental data between 300 and 400K, where an important part comes from the anharmonicity[4].

Secondly, we investigated the diffusion of protons in hydroxides under pressure. In particular, layered hydroxide minerals have immediate interest in chemistry, in the industry (glass, cements) and in geosciences (water retainer, mantle crust). These systems were simulated using Centroid MD[3]. We found interesting features such as: H atom layers stack into a single quasi 2D-layer at high pressure; the diffusion process is fastened by tunnelling and zero point energy effects; and the transport of protons is correlated due to H...H interactions[5].

References

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