Nuclear quantum effects by accelerated molecular dynamics and quantum Monte Carlo

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We use the recently proposed accelerated molecular dynamics scheme[1] to sample in an efficient way the finite temperature partition function of quantum distinguishable nuclei - exchange effects are neglected - interacting within the Born-Oppheneimer energy surface, namely the electrons are frozen in their instantaneous ground state at fixed nuclear positions. Within the DFT approximation for the electronic ground state, the method represents a clear improvement even when compared with state-of-the-art techniques based on the transformation to normal mode coordinates[2] and the recent generalization of the Ornstein–Uhlenbeck dynamics[3]. Within quantum Monte Carlo methods, and the recent progress for the computation of nuclear forces within variational Monte Carlo, the proposed technique allows a remarkable speed-up, by several order of magnitudes, i.e. by an extra factor proportional to the number of beads used to discretize the imaginary time in the corresponding path integral, implying that the exact continuous time limit of the path integral (infinite number of beads) is achievable essentially at no computational cost. In this way the quantum Monte Carlo description of quantum nuclear effects can be obtained basically at the same price of a corresponding calculation with classical nuclei. We test this method on hydrogen at high pressure and we compare the simulations with existing results for the liquid liquid transition at 1200K and around 200Gpa. We show that, thanks to the accelerated dynamics, realistic simulations based on QMC are nowadays possible and competitive with DFT ones, especially in the quantum case.

[1] G. Mazzola and S. Sorella Phys. Rev. Lett. **118**, 016703 (2017).

[2] M. Ceriotti, M. Parrinello, T. M. Merkland, and D. E. Manousopolis, J. Chem. Phys., 133, 124104 (2010).

[3] Felix Mouhat, Sandro Sorella, Rodolphe Vuilleumier, Antonino Marco Saitta, and Michele Casula, J. Chem. Theory and Computation, DOI: 10.1021/acs.jctc.7b00017 (2017).