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Accurate Energies for Molecular Dynamics Simulations of Molecules and Liquids[1]

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A method is presented to treat electrons within the many-body quantum Monte Carlo (QMC) approach "on-the-fly" throughout a molecular dynamics (MD) simulation. Our approach leverages the large (10–100) ratio of QMC electron to MD ion motion to couple the stochastic, imaginary-time electronic and real-time ionic trajectories. This continuous evolution of the QMC electrons results in highly accurate total energies for the full dynamical trajectory at a fraction of the cost of conventional, discrete sampling. We show that this can be achieved efficiently for both ground and excited states with only a modest overhead to an ab initio MD method. The accuracy of this dynamical QMC approach will be demonstrated for a variety of systems, phases, and properties, including optical gaps of hot silicon quantum dots, dissociation energy of a single water-molecule, and heat of vaporization of liquid water. We also evaluate forces on ions along the MD trajectories in QMC and compare these with forces computed by other methods. Finally, we carry out a molecular dynamics simulation completely within the QMC framework for both forces and energies. This work was performed under the auspices of the US Department of Energy by the University of California at the LLNL under contract no W-7405-Eng-48.

[1]in collaboration with Lubos Mitas, Lucas Wagner, and Giulia Galli.