Ab initio Molecular Dynamics from Conditional Wave Functions

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A rigorous trajectory-based formulation of the electron-nuclear dynamics of molecules and solids is developed based on replacing electronic and nuclear degrees of freedom in the complete-system wave function by the actual configuration of quantum trajectories. The resulting entitites, called conditional wave functions [1], are used to split the time-dependent Schrödinger equation into electronic and nuclear equations of motion. The formalism does not rely on any tracing-out of the electronic degrees of freedom, which makes it per-se an approach beyond mean-field. Moreover, based on quantum hydrodynamics, it constitutes a rigorous way of mixing waves and trajectories, i.e. quantum trajectories provide the correct expectation value of the nuclear observables. Further, its realization is based on the propagation of electronic and nuclear equations of motion without prior knowledge of the involved Born-Oppenheimer potential-energy surfaces. The exact splitting of electronic and nuclear degrees of freedom presented here lends itself as a rigorous starting point for the systematic developement of approximations. Preliminary results show that even the simplest algorithm accurately captures non-adiabatic dynamics in the limit of nonspreading electron-nuclear wave functions. Far from this regime the simplest algorithm fails to preserve energy conservation, and a way to improve the method is proposed. By imposing a factorizable solution of the complete-system wave function, a connection between our formalism and the time-dependent potential-energy surfaces found in [2] is also established. Further work will be devoted to derive a set of conditional equations starting from the multicomponent time-dependent Kohn-Sham system [3].

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[2] X. Oriols, Phys. Rev. Lett **98**, 066803 (2007).
[3] O. Butriy, *et al.*, Phys. Rev. A **76**, 052514 (2007).