

Mapping Hamiltonian Dynamics of Open Quantum-Classical Systems

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Mixed quantum-classical methods, where a quantum subsystem is coupled to a classical environment, provide a means to study the dynamics of complex open quantum systems that cannot be studied easily by other means. A brief overview of the quantum-classical Liouville equation, along with illustrations of its application to a number of quantum reaction rate and energy transfer problems, will be given. Applications include proton transfer in molecular solvents and clusters and population transfer near a conical intersection. In this description the quantum subsystem may be represented in any basis and the choice of basis determines the algorithm used to simulate the dynamics.

The mapping basis provides a continuous description of discrete quantum states and offers the possibility to construct effective simulation schemes that do not involve surface-hopping dynamics [1-2]. A number of aspects of this representation will be discussed [3]. By defining projection operators onto the mapping states corresponding to the physical quantum states, it will be shown that the mapping quantum-classical Liouville operator commutes with the projection operator so that the dynamics is confined to the physical space. It will also be shown that a trajectory-based solution of this equation can be constructed that requires the simulation of an ensemble of entangled trajectories. An approximation to this evolution equation which admits a solution in an ensemble of independent trajectories does not commute with the projection operator and the dynamics may take the system outside the physical space. The dynamical instabilities, utility and domain of validity of this approximate dynamics will be described, and connections with other methods will be made. Using these methods, exact and approximate simulation results on energy transfer and coherence for a number of systems will be presented.

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- [3] A. Kelly, R. van Zon, J. M. Schofield and R. Kapral, unpublished (2012).