Semiclassical Nonadiabatic Dynamics with Quantum Trajectories

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Despite recent progress in exact quantum dynamics, approximate methods are needed in order to model many-body processes. Quantum dynamics on coupled electronic states have been approached by various techniques. Among these, trajectory-based (mean-field, trajectory surface hopping) methods are very popular, because they are intuitive and relatively easy to implement. However, these methods do not describe properly the phases developed by the nuclear wave packets moving on the electronic potential energy surfaces (PES). The phase coherence plays a crucial role in mediating the population transfer from one electronic state to the other.

In the last five years, quantum hydrodynamics has emerged[1,2] as a possible contender among exact quantum dynamics methods. In the version proposed by Wyatt, the Quantum Trajectory Method (QTM), the quantum probability fluid is divided into a finite number of elements (also called "particles") that evolve under the influence of combined classical and quantum forces. QTM is formally exact in the limit of an infinite number of particles. Although the method seems very attractive, its future depends on the ability to accurately compute the *non-local* quantum potential on the moving grid defined by the particles, a task that can be very difficult in certain situations (near wave function nodes in particular).

Recently, QTM has been extended to electronically nonadiabatic collisions by Wyatt *et al.*[3] In this formally exact quantum-mechanical algorithm for electronic transitions, a swarm of coupled quantum trajectories evolves *on each one of* the electronic PES. The number of trajectories on each PES is conserved and no trajectory surface hopping is involved; rather, probability density and wave function phase information is transferred continuously from one electronic state to the other.

In this presentation, we report on approximate implementations of the nonadiabatic QTM. A local harmonic expansion of the classical potential is utilized, in the spirit of the works by Heller[4] and Metiu.[5] As a result, the evaluation of the quantum potentials is drastically simplified. The method gives excellent results on a model problem[6] of two wave packets propagating simultaneously through a curve crossing with, in particular, an excellent conservation of coherence. The method conserves most of the nice features of the formally exact nonadiabatic QTM, while using almost exclusively well known classical trajectory propagation techniques.

Moreover, as suggested recently by Tully,[7] it is conceivable to drop the quantum potentials altogether in the nonadiabatic QTM. Thus, the nuclear motion is propagated classically on each PES, while density probability is exchanged between electronic states. This technique is implemented here, on a simple passage through a curve-crossing, with encouraging results. Since the hydrodynamics phase space is distinct from the usual Wigner phase space, further investigations will be needed in order to connect the present zero quantum potential limit with standard classical trajectory simulations.[8]

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