Effective Quantum-Classical Dynamics in an Open Quantum Environment

Kazutomu Shiokawa and Raymond Kapral
Chemical Physics Theory Group, Department of Chemistry,
University of Toronto, Toronto, ON M5S 3H6, Canada

Abstract

In this paper, we investigate some of the circumstances under which an open quantum system can be described using mixed quantum-classical dynamics. Quantum-classical dynamics is used to study condensed phase many-body systems, especially in the context of methods for treating non-adiabatic dynamics. In the studies presented here, we consider a composite quantum mechanical system AC comprising two coupled subsystems A and C; subsystem C is assumed to be in direct contact with a thermal quantum mechanical bath B. Systems with this structure can arise in condensed phase dynamics where certain quantum degrees of freedom (A), for example, those associated with protons or electrons, may interact directly with neighboring solvent molecules (C), which in turn interact with the rest of the solvent (B). It is interesting to determine if the composite system may be treated as a mixed quantum-classical system where the dynamics of subsystem C, which is in direct contact with the heat bath, is classical in character while subsystem A retains its quantum nature. Some aspects of the dynamics of such quantum-classical composite systems have been investigated.

In order to investigate this problem we study a simple model system where subsystem A depends on spin degrees of freedom and subsystem C is a single harmonic oscillator bilinearly coupled both to subsystem A and the bath. The bath is a collection of independent harmonic oscillators. While this is a highly simplified model of the realistic systems discussed above, it does capture some essential features of real coupled systems and is amenable to detailed analysis. Due to its interaction with the bath, the dynamics of subsystem C is dissipative and executes brownian motion. The brownian motion of a quantum particle governed by different potential functions and immersed in a thermal harmonic oscillator bath has been studied extensively by influence functional methods. The character of its dynamics is determined by the system-bath coupling and the spectral density and temperature of the bath. In the composite system we study, the dynamics of the C subsystem oscillator is also influenced by the quantum dynamics of subsystem A. The dynamics of subsystem A is more complicated. It is also dissipative but its energy must be transmitted through subsystem C to the bath.

Our results on the applicability of mixed quantum-classical dynamics are based on the nature of decoherence in the coupled system: when one subsystem behaves quantum mechanically and the other classically, there must be a mechanism making the former decohere slowly and the latter quickly.

Using influence functional methods, we have shown for our simple model system that the decoherence time scales that characterize the A and C subsystems can differ significantly. In particular, in the limit of nonadiabatic dynamics we have identified the following three regimes: (1) the full quantum regime where both the A and C subsystems behave quantum mechanically; (2) the quantum-classical regime where subsystem A maintains coherence owing to its indirect coupling to the bath, while C has lost its coherence and behaves effectively classically; (3) the classical regime where the quantum coherence of both the A and C subsystems has been lost and the composite AC subsystem exhibits effectively classical dynamics.

Our results show that for an Ohmic bath one may observe quantum-classical dynamics for some finite time interval, but eventually the decoherence factors for both the A and C subsystems increase, leading to classical behavior in the AC subsystem. For a super-Ohmic bath the strong increase in the C subsystem decoherence factor and the weaker increase of that for A implies that one may observe quantum-classical evolution for a longer initial time interval to a high degree of accuracy before classical behavior ensues (see Fig. 4b). Furthermore, since the decoherence factor of subsystem A saturates at a finite value which depends on the system parameters, it is possible to find regimes where quantum-classical evolution holds indefinitely because the A decoherence factor is small for all times. Thus, while all three regimes are found to exist for an Ohmic bath for all parameter ranges, only regimes (1) and (2) exist for a 3D super-Ohmic bath for some parameter choices.

In most applications where a condensed phase environment is modeled by a bath of harmonic oscillators an Ohmic spectral density is assumed with the dissipation coefficient determined from experiment. Super-Ohmic spectral densities have also been used to model vibrational relaxation by acoustic phonons in a crystalline host or systems where a degree of freedom couples linearly through its momentum to an effective isotropic elastic medium.

We also saw that a different choice of initial conditions will modify above picture. When the initial condition for C is chosen to be a pure gaussian coherent state, CB can no longer be considered to be a thermal bath and the coherence of A will be lost in a shorter time scale than times given by the inverse characteristic frequency of C.