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Towards an understanding of escape rate and state dependent diffusion for a quantum dissipative system

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ABSTRACT

We address the stochastic dynamics of an open quantum system coupled to a heat reservoir that is driven out of thermal equilibrium by an external noise. By constructing Langevin and Fokker–Planck equations, we obtain the rate of decay from a metastable state of the system when the dissipation is state dependent. We discuss the effects and consequences of the non-linear interaction(s) stemming out of the system-bath coupling alongside the modulation of the bath by an external noise on the rate expression. We demonstrate that the temperature dependence of the escape rate is not only embedded in the so-called Arrhenius type factor, the second exponential factor also includes the temperature dependence. The last effect has a purely quantum origin. Interestingly, we also envisage that this quantum effect is entangled with dissipation. The results offer a basis for clarifying the relationship between the dissipation and exponential factor of the obtained rate expression.

1. Introduction

The last few decades have envisaged a paradigm shift in the understanding of the non-equilibrium dynamics of open quantum systems encompassing many branches of chemical sciences (such as chemical reactions in solution, and tunneling in biosystems, to name but a few). The celebrated system-reservoir model [1–10], central to such diverse fields, has found extensive and deep-rooted implementation in enlightening a plethora of unknown facets associated with the quantum dissipation phenomena that makes its appearance frequently in a variety of contexts [11–19]. This model has become an extremely reliable, as well as a handy tool for the physicists, chemists and biologists to unravel the as of yet unknown aspects pertaining to the microscopic dynamical behavior in a host of systems. In this context, the most popular approach is to model the situation in a manner so as to deal with an interaction between the system and the associated reservoir with the later being linear in both system as well as bath coordinates. The dynamical equation, i.e., Langevin equation, in such systems is shaped by the exact form of interaction with the bath, since this interaction in turn determines both-fluctuation and the associated dissipation. The common source of origin of both the noise and the consequent dissipation essentially entangles the two via the celebrated fluctuation–dissipation relation [20]. However, this triviality is lost whenever the coupling between the system and the reservoir is linear in bath coordinates but nonlinear in system coordinates. Such situations are characterized by the genesis of multiplicative noise [21–30] and nonlinear dissipation in the form of coordinate dependent friction. The nonlinearity in the system coordinates that creeps in as a consequence of the aforesaid, however, preserves the original structure of the fluctuation–dissipation relation, culminating in the system to attain the correct thermal equilibrium eventually. Several research groups have explored the role and consequence of the space dependent friction in the classical regime, for example, in the study of charge transfer reactions in polar media and activated rate processes in overdamped regime [31–35], fluctuation induced transport [36,37], stochastic resonance [38–41], noise induced transition [42,43], vibrational and Raman spectroscopy [44] and so on. Interestingly enough, in all of the contexts mentioned above, it has been tacitly assumed that the associated heat bath is in thermal equilibrium and consequently the Langevin equation that corresponds to the situation is one for a thermodynamically closed system. Apart from a few exceptions [45–47], a Langevin formulation with state dependent dissipation and multiplicative noise processes for a thermodynamically open system has drawn little attention. In Ref. [46], Shepherd and Hernanadez introduced separate stochastic forces, one for thermalization and the other accounting for the open interaction with an external bath. The latter was assumed to be thermalized at the same temperature as the system and this required renormalization of the friction rather

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than the effective temperature as pursued in the current work. However, it is illustrative of the balance of forces that is required to maintain the fluctuation–dissipation theorem. In the current work, Hernandez and coworkers [47] investigate a generalized chemical process in which the nonequilibrium behavior of the chosen subsystem is influenced by a change in temperature of the environment that is in turn influenced by the response of the subsystem. In such a case, the environment itself can also persist in a nonequilibrium state.

In several situations, especially at low temperatures, it is generally difficult to develop a consistent theory of dissipation relying on the classical Brownian motion, since such a treatment is devoid of quantum effects. In nano-scale and biological systems the quantum noise that stems out of quantum fluctuations is also of immense significance. A plethora of aspects in various fields have come to the fore in recent times that establish the ubiquity of the quantum treatment. The reversal of magnetization owing to quantum tunneling [48,49] and the consequent Neel relaxation [50], the noise-assisted tunneling and transfer of electrons and quasi-particles [13], and the flux quantum transitions in a SQUID [35,51] are certain prominent manifestations of the quantum effects. Very recently, a beautiful realization of Kramers barrier crossing as a cooling machine has been put forward by Schiff and Nitzan [52].

Quite contrary to the classical regime, consistent and tractable equations of motions in the quantum domain in the dissipative range at low temperatures are difficult to conceive [12]. During the early eighties Caldeira and Leggett [2,3] pioneered the treatment of quantum dissipation based on a linear interaction between the system and the reservoir. This approach was soon to envisage numerous applications and implementations spanning a host of areas in chemical and condensed matter physics [2,3,12,53] that encompass quantum interference devices, polaron in a magnetic field, quantum decay processes and the likes. It is only recently that the study of the physics of non-linear system reservoir coupling in a quantum system has been started. Bao [34] has observed that quantum dissipation can reduce the appearance of metastable state(s) [54] and barrier drift in a double well potential. Tanimura and coworkers [5] have modeled nonlinear coupling while studying the elastic and inelastic relaxation mechanisms and their roles in Raman and infrared spectra. Quantum transport originating from a state dependent diffusion in a periodic potential has been investigated [30]. A scrutiny of the nature of nonlinear coupling (say, linear in bath coordinates but quadratic in system coordinates) reveals the fact that, in contrast to the linear case which induces displacement only, the nonlinear one induces fluctuations of the system potential. The effect of this fluctuation has been addressed in both spin–spin and spin–lattice relaxation processes [55–58]. Apart from making the effective potential nonlocal, the fluctuation in the system potential due to nonlinear coupling makes the diffusive process inhomogeneous in nature. This aspect has a pivotal role to play in the context of quantum rate processes, and exploring the nature of decay of a metastable state(s) as a result of inhomogeneous quantum diffusion is thus a challenging task. In addition to these, we must point out that the path integral based representation provides an exact expression for the time dependent density matrix, but numerical evaluations are prohibitive [59]. However, considerable progress has been achieved in the development of master equation [60] and the quasiadiabatic propagator approach [61]. At this point we want to emphasize that Ankerhold et al. [14,15] have proposed a transparent generalization of Smoluchowksi equation (via the path integral formulation of quantum dissipative systems) to the low temperature quantum domain and demonstrated that quantum fluctuations may appear at relatively elevated temperatures and substantially influence the quantum dynamics. In this context we also mention the related developments for strongly condensed phase systems by various group [16,62].

The present work embodies a development towards the quantum regime and simultaneously retains the classical structure of the quantum Langevin equation. Here we address the problem of quantum Langevin equation (stochastic dynamics) with multiplicative noise and state dependent diffusion for a thermodynamically open system to explore the nature of nonlinear coupling and modulation of heat bath with its consequences, specifically in the context of barrier crossing dynamics. We consider a system reservoir model where the associated bath is not in thermal equilibrium but is modulated by an external colored noise and the system is nonlinearly coupled with the heat bath, thereby resulting in a nonlinear multiplicative quantum Langevin equation with state dependent dissipation. When the reservoir is modulated by an external noise, it is likely that it induces fluctuations in the polarization of the reservoir [45]. Due to the presence of external noise, one may expect that the nonequilibrium situation created by modulating the bath may make its presence felt in the barrier crossing dynamics. A number of different situations depicting the modulation of the heat bath may be physically relevant. For example, we may consider a simple unimolecular conversion $x \to y$, say, an isomerization reaction, carried out in a photochemically active solvent. The growth of living polymerization [63,64] is another such example. Since the fluctuations in the light intensity result in fluctuation in the polarization of the solvent molecules, the effective reaction field around the reactants gets modified. For an excellent review in this context see Ref. [65].

It is important to mention the fact that obtaining the quantum reaction rate and studying the quantum transport phenomena in macroscopic system is a difficult and challenging task. Many workers resort to a classical or quasiclassical approach as a tool for studying the dynamics. The impressive *state-of-the-art* computations on dissipative systems [66] remain limited and are not readily generalized to realistic systems [67]. A formally exact description of an open quantum system is valid for all temperatures and damping strength is provided by the path integral approach initiated by the work of Feynman and Vernon [68]. Important achievements have been made in the last few years with the emergence of advanced path integral Monte-Carlo (PIMC) techniques [69]. Mühlbacher et al. [69] have suggested a PIMC scheme which provides an effective avenue to model the nonequilibrium dynamics of correlated electron transfer even over longer time scales. However, despite tremendous progress, still various rather fundamental questions need to be elucidated. Recently, formulation of a quantum Langevin equation based on the *c*-number approach [6] has been proposed where the authors have used a coherent state representation of the noise operator and a canonical thermal Wigner distribution [70] of the bath oscillators. The formalism and its different variants have been successfully applied to explain several aspects of reaction rate theory in condensed phases [6]. Prompted by its success, we explore in this paper a physically motivated formalism in the context of quantum mechanical Langevin equation with state dependent dissipation and multiplicative colored noise to study the barrier crossing dynamics. Thus, at the focus of our present work are the concomitant thermally activated escape rates far from equilibrium (nonequilibrium) regime. It is worth stressing here that although there are various developments to deal with the Langevin dynamics with additive noises in the classical context [71], despite the various methodological developments and corresponding implementations, searching for methods capable of reliable and correct description of the phenomena associated with the multiplicative colored noise still remains a challenge in the realm of chemical physics. The problem becomes even more challenging in the quantum context. Here, we want to mention that to investigate the role