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External-noise-driven bath and the generalized semiclassical Kramers theory

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We address the issue of a system that has been tacitly made thermodynamically open by externally driving the associated heat bath in an attempt to gain better insight regarding many physical situations that are akin to this problem. This work embodies the study of the quantum effects in the rate of decay from a metastable state of a Brownian particle which is in contact with a correlated noise-driven bath. We do this by initiating from a suitable system-reservoir model to derive the operator-valued Langevin equation. This further leads us to the corresponding *c*-number analog that includes quantum effects in leading order. Suitable mathematical treatment culminates in the quantum Fokker-Planck equation, the solution to which yields the rate expression. Finally, we put this to thorough numerical analysis.

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I. INTRODUCTION

Since Kramers proposed the diffusion model for chemical reactions in terms of the theory of the Brownian motion in phase space [1], the model and several of its variants became ubiquitous in many areas of physics, chemistry, and biology for understanding the nature of activated processes in classical [2–7], semiclassical, and quantum systems [8–11] in general. These have become the subject of several articles [12–16] and monographs [17,18] in the recent past. The majority of these treatments concern essentially with an equilibrium thermal bath at a finite temperature that simulates the reaction coordinates to cross the activation energy barrier and the inherent noise of the medium originates internally. This implies that the dissipative force, which the system experiences in the course of its motion in the medium, and the stochastic force arising on the system as a result of the random impact from the constituents of the medium arise from a common mechanism. It is therefore not difficult to anticipate that these two entities get related through a fluctuation-dissipation relation [17,18]. These systems are generally classified as being thermodynamically closed, in contrast to the systems driven by external noise(s) in nonequilibrium statistical mechanics [19]. However, when the reservoir is modulated by an external noise, it is likely that this relation gets affected in a significant way. The modulation of the reservoir crucially depends on its response function and this makes us to further investigate a connection between the dissipation of the system and the response function of the reservoir due to external noise(s) from a microscopic point of view.

In the present paper, we explore the above connection in the quantum regime, in the context of activated rate processes, when the reservoir is modulated by an external stationary Gaussian noise. Specifically, we would like to explore the role of reservoir response as a function of external noise on the system dynamics and to calculate the generalized Kramers' rate for the steady state of this nonequilibrium open system within the framework of the quantum Langevin equation.

The last few decades have witnessed an extensive study by several research groups [11,20–25] on the problem of the quantum Langevin equation for a thermodynamically closed system due to its frequent appearance in the course of modeling of various phenomena, particularly in the field of laser and optics [20–23], signal processing [24,25], noise-induced transport [26–29], spectroscopy, [30–33] etc. In the recent years, the subject has gained considerable interest due to a vast experimental progress which allows for the tailoring and manipulation of quantum matter. In mesoscopic physics, for instance, superconducting circuits have been realized to observe coherent dynamics and entanglement [34]. A similar advancement has been achieved on molecular scales with the detection of interferences in wave-packet dynamics and the control of population of the specific molecular states [35]. Typically, these systems are in contact with a large number of environmental degrees of freedom, for example, electromagnetic modes of the circuitry or residual vibronic modes which give rise to decoherence and relaxation [36].

For microscopic description of additive noise and linear dissipation that are related by fluctuation-dissipation relation, the quantum-mechanical system-reservoir linear coupling model is well established. The standard treatment of quantum dissipation based on linear interaction between the system and the reservoir was put forward in early 1980s by Caldeira and Leggett [37] which was widely applied in several areas of condensed matter and chemical physics. Later a number of interesting approaches to quantum theory of dissipative rate processes such as dynamical semigroup method for evolution of density operator were proposed in the 1970s to treat quantum nonlinear phenomena with considerable success. The method which received major appreciation in the wide community of physicists and chemists is the real-time functional integrals [9]. Notwithstanding the phenom-

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enal success of the functional-integral approach, it may be noted that compared to the classical Kramers' theory, the method of functional integrals for the calculation of escape rate rests on a fundamentally different footing. While the classical theory is based on the differential equation of motion for evolution of the probability distribution function of a particle executing Brownian motion in a force field, the path-integral method relies on the evolution of quantum partition function of the system interacting with the heat bath consisting of harmonic oscillators.

The standard approach to open quantum systems constitutes obtaining the reduced dynamics of the system of interest by tracing out the reservoir degrees of freedom from the conservative system-plus-reservoir dynamics. Alternatively, the program can be carried out through path-integral expressions for the reduced density matrix [38]. The distinguishing feature of the dissipative path integrals is an influence functional which describes self-interactions nonlocal in time. Hence, a simple quantum-mechanical analog to the classical Langevin equation is not known. Commonly used equations, such as the master or Redfield equation [39] in the weak-coupling case and the quantum Smoluchowski equations [40], rely on a perturbation theory. The recent work of Ankerhold *et al.* [41] analyzes the case of the quantum Smoluchowski equation in the strong fiction regime at low temperatures starting from an exact path-integral expression. In intermediate domain, the quantum Monte Carlo techniques have been posited for tight-binding systems, but achievable propagation times are severely limited by the dynamical sign problem [42,43]. Recently, it has been shown that the influence functional can be exactly reproduced through stochastic averaging of a process without explicit memory [44,45]. The formulation turned out to be particularly efficient for weak to moderate friction and low temperatures [45,46], a regime which lies beyond the validity of the Redfield equations, on the one hand, and beyond the applicability of the Monte Carlo schemes, on the other [42,43]. For nonlinear systems, the main objection of the Monte Carlo simulation is that the convergence of the stochastic average for relatively long time is still an unsolved problem, barring some progress for spin boson systems, by using hierarchic approaches to quantum memory terms [47]. A reliable and efficient method to tackle the dissipation in quantum domain is still missing. In this paper, we address the issue of the long lasting problem of quantum dissipative dynamics of a thermodynamically open system, where the associated heat bath is not in thermal equilibrium, implementing the standard classical statistical mechanical tools that are particularly used in the context of noise-induced transport.

The physical situation that we consider here is the following: at $t=0$, the reservoir is in thermal equilibrium with the system, while at $t=0_+$, an external noise agency is switched on to modulate the heat bath [48,49]. This modulation makes the system thermodynamically open. Using a standard method, we then construct the operator Langevin equation for an open system with linear system-reservoir coupling.

To proceed with the discussion in an appropriate perspective, we begin with the note that in an earlier work [50], Ray Chaudhuri *et al.* studied the dynamics of a metastable state of a system linearly coupled to a heat bath which is driven by an external noise in the classical regime. The work [50] concerns a derivation of the generalized Langevin and the corresponding Fokker-Planck equations to study the escape rate from a metastable state in the moderate to large damping regime. In the present work, we have focused on the dynamics of the corresponding situation in a quantum-mechanical context. The aim of the present paper is thus to explore the associated quantum effects in the decay rate of a particle (from a metastable state) which is in contact with a correlated noise-driven bath. However, an exploration in the quantum regime has been done [51] with the bath in equilibrium where a c-number generalized quantum Langevin equation has been derived. The present work is different in the sense that it is quantum mechanical as well as the bath is being externally modulated via a fluctuating force field.

The layout of the paper is as follows. In Sec. II, starting from a system-reservoir model, we arrive at the operator-valued Langevin equation for an open quantum system where the associated heat bath is modulated by an external Gaussian noise with arbitrary decaying memory kernel. Then, we obtain the c-number analog of this operator equation. In Sec. III we calculate the quantum correction terms and we derive the quantum Fokker-Planck equation in Sec. IV. Section V comprises of the calculation of escape rate by solving the steady-state Fokker-Planck equation incorporating the quantum effects. The dependence of the escape rate on various system parameters has been discussed in Sec. VI. The paper is concluded in Sec. VII.

II. MODEL: LANGEVIN DESCRIPTION OF QUANTUM OPEN SYSTEM

To start with, we consider a particle of unit mass coupled to a reservoir comprised of a set of harmonic oscillators with characteristic frequencies $\{\omega_j\}$. Initially ($t=0$), the system and the reservoir are in thermal equilibrium at temperature T. At $t=0_+$, an external noise is switched on which modulates the bath. This is described by the Hamiltonian

$$\hat{H}=\frac{\hat{p}^2}{2}+V(\hat{q})+\sum_{j=1}^{N}\left\{\frac{\hat{p}_j^2}{2}+\frac{1}{2}\omega_j^2(\hat{x}_j-c_j\hat{q})^2\right\}+\hat{H}_{int}, \quad (1)$$

where $\hat{q}$ and $\hat{p}$ are the coordinate and momentum operators of the system and $\{\hat{x}_j,\hat{p}_j\}$ are the set of coordinate and momentum operators for the bath oscillators. The masses of the bath oscillators are assumed to be unity for convenience. The system particle is bilinearly coupled to the bath oscillators through the coupling constant c_j. The last term in Eq. (1), $\hat{H}_{int}=\Sigma_j\kappa_j\hat{x}_j\epsilon(t)$, represents the fact that the bath is driven by an external noise $\epsilon(t)$, which is assumed to be stationary and Gaussian. $\epsilon(t)$ is a classical noise which obeys the statistical properties that the mean of $\epsilon(t)$ is zero and the two-time correlation function is a decaying function of time, i.e.,

$$\langle\epsilon(t)\rangle=0$$

$$\text{and}\quad \langle\epsilon(t)\epsilon(t')\rangle=2D\psi(t-t'). \quad (2)$$

In Eq. (2), the average is taken over each realization of $\epsilon(t)$ and ψ is some arbitrary decaying memory kernel. $V(\hat{q})$ is the potential operator. The coordinate and momentum operators satisfy the standard commutation relation,

$$[\hat{q},\hat{p}] = i\hbar$$

$$\text{and} \quad [\hat{x}_j,\hat{p}_k] = i\hbar\delta_{jk}, \tag{3}$$

and D is the strength of the external noise $\epsilon(t)$. Using the standard procedure we eliminate the bath variables in usual manner [17,52] to obtain the operator-valued Langevin equation for the system variables as

$$\dot{\hat{q}} = \hat{p},$$

$$\dot{\hat{p}} = -V'[\hat{q}(t)] - \int_0^t dt'\,\gamma(t-t')\hat{p}(t') + \hat{\eta}(t) + \pi(t)\hat{I}, \tag{4}$$

where $\hat{I}$ is the unit operator and

$$\pi(t) = -\int_0^t dt'\,\varphi(t-t')\epsilon(t'), \tag{5}$$

$$\gamma(t) = \sum_{j=1}^{N} c_j^2\omega_j^2 \cos \omega_j t, \tag{6}$$

$$\varphi(t) = \sum_{j=1}^{N} c_j\omega_j\kappa_j \sin \omega_j t, \tag{7}$$

and $\hat{\eta}(t)$ is the internal thermal noise operator given by

$$\hat{\eta}(t) = \sum_{j=1}^{N} c_j\omega_j^2\left\{[\hat{x}_j(0) - c_j\hat{q}(0)]\cos \omega_j t + \frac{\hat{p}_j(0)}{\omega_j}\sin \omega_j t\right\}, \tag{8}$$

with the statistical properties

$$\langle \hat{\eta}(t)\rangle_{QS} = 0 \tag{9}$$

and

$$\frac{1}{2}\langle \hat{\eta}(t)\hat{\eta}(t') + \hat{\eta}(t')\hat{\eta}(t)\rangle_{QS} = \frac{1}{2}\sum_{j=1}^{N} c_j^2\omega_j^2\hbar\omega_j \coth\left(\frac{\hbar\omega_j}{2k_BT}\right)\cos \omega_j(t-t'). \tag{10}$$

At this juncture we wander a bit from the usual track and highlight the features of $\pi(t)$. Several factors, like the normal mode density of the bath frequencies, the coupling of the system with the bath, the coupling of the bath with the external noise, and the external noise itself, determine the statistical properties of $\pi(t)$. A scrutiny of Eq. (5) reveals the familiar linear relation between the polarization and the external field with $\pi(t)$ and $\epsilon(t)$ playing the former and the latter roles, respectively. With this in view, one may envisage $\varphi(t)$ as a response function of the reservoir due to external noise $\epsilon(t)$. Although $\pi(t)$ is a forcing function stemming out from an external noise, it has a difference from a direct driving force acting on the system, and this aspect is clearly borne out by the mathematical structure of $\pi(t)$. This subtle difference originates from the actual nature of the bath properties (rather than system characteristics, as is traditionally seen), and this is clearly reflected in relations (5) and (7).

It is important to mention that the operator Langevin equation [Eq. (4)] contains both—an internal noise $\eta(t)$ and the *dressed* noise $\pi(t)$ due to the modulation of the bath by the external noise $\epsilon(t)$, and thus resembles a quantum Langevin equation with an external field. This type of work has already been reported in literature [53]. In the absence of any external modulation, the above quantum Langevin equation boils down to the standard quantum Langevin equation which applies to an equilibrium thermal bath and has already been discussed in a comprehensive paper [14].

Here, $\langle\cdots\rangle_{QS}$ implies quantum statistical average on the bath degrees of freedom and is defined as

$$\langle\hat{O}\rangle_{QS} = \frac{\mathrm{Tr}\left[\hat{O}\exp\left(-\frac{H_B}{k_BT}\right)\right]}{\mathrm{Tr}\left[\exp\left(-\frac{H_B}{k_BT}\right)\right]} \tag{11}$$

for any bath operator $\hat{O}(\hat{x}_j,\hat{p}_j)$ where

$$H_B = \sum_{j=1}^{N}\left[\frac{p_j^2}{2} + \frac{1}{2}\omega_j^2(\hat{x}_j - c_j\hat{q})^2\right] \quad \text{at } t=0. \tag{12}$$

At this juncture we explore an alternative possibility that arises out of the physical situation where we could have redefined Eq. (8) by an alternative noise term $\zeta(t)$ as

$$\hat{\zeta}(t) = \sum_{j=1}^{N} c_j\omega_j^2\left\{\hat{x}_j(0)\cos \omega_j t + \frac{\hat{p}_j(0)}{\omega_j}\sin \omega_j t\right\}. \tag{13}$$

This would lead to the modification of the Langevin equation [Eq. (4)] to the form

$$\dot{\hat{q}} = \hat{p},$$

$$\dot{\hat{p}} = -V'[\hat{q}(t)] - \int_0^t dt'\,\gamma(t-t')\hat{p}(t') + \hat{\zeta}(t) - \gamma(t)\hat{q}(0) + \pi(t)\hat{I}. \tag{14}$$

We note that the above equation is equivalent in form with Eq. (2.10) of Ford and O'Connell [15]. In this case, the quantum statistical average of $\hat{\zeta}(t)$, that is, $\langle\hat{\zeta}(t)\rangle_{QS}=0$, provided we choose to work with an initial bath distribution of the form

$$H_B = \sum_{j=1}^{N}\left[\frac{\hat{p}_j^2}{2} + \frac{1}{2}\omega_j^2\hat{x}_j^2\right] \quad \text{at } t=0, \tag{15}$$

that is, to say that the bath remains in equilibrium in the absence of the system. However, in the current formulation we have addressed the problem tracing the path as suggested in [52] and have chosen to work in a situation where the bath is in thermal equilibrium in the presence of the system. The reason for this choice for us, in the present context, is obviated by our focus to explore the fluctuation induced barrier crossing dynamics of the Langevin particle rather than on its equilibration. Additionally, we would like to point out that we are neither looking at the present problem as an initial value quantum Langevin equation nor we are making any attempt to explore how the equilibration takes place [54], rather we try to envisage the barrier crossing dynamics in the high-temperature quantum regime. Had we visualized this as an initial value problem, we would have adopted the idea as put forth in [15]. As a consequence we have incorporated the term $\gamma(t)\hat{q}(0)$ in our noise term [Eq. (8)] so that Eqs. (9) and (10) remain valid throughout. For a detailed review on this aspect we refer the reader to Chap. 3 of Ref. [17].

Let us carry out a quantum-mechanical averaging of the operator equation [Eq. (4)] to get

$$\langle \dot{\hat{q}} \rangle_Q = \langle \hat{p} \rangle_Q, \tag{16}$$

$$\langle \dot{\hat{p}} \rangle_Q = -\langle V'[\hat{q}(t)] \rangle_Q - \left\langle \int_0^t dt' \, \gamma(t-t') \hat{p}(t') \right\rangle + \langle \hat{\eta}(t) \rangle_Q + \pi(t), \tag{17}$$

where the quantum-mechanical average $\langle \cdots \rangle_Q$ is taken over the initial product separable quantum states of the particle and the bath oscillators at $t=0$, $|\varphi\{|\alpha_1\rangle|\alpha_2\rangle \cdots |\alpha_N\rangle\}\rangle$. Here, $|\varphi\rangle$ denotes any arbitrary initial state of the system and $\{|\alpha_j\rangle\}$ corresponds to the initial coherent state of the jth bath oscillator. $\langle \hat{\eta}(t) \rangle_Q$ is now a classical-like noise term, which, because of quantum-mechanical averaging, in general, is a nonzero number and is given by

$$\langle \hat{\eta}(t) \rangle_Q = \sum_{j=1}^{N} \left[c_j \omega_j^2 \left\{ [\langle \hat{x}_j(0) \rangle_Q - c_j \langle \hat{q}(0) \rangle_Q] \cos \omega_j t + \frac{\langle \hat{p}_j(0) \rangle_Q}{\omega_j} \sin \omega_j t \right\} \right]. \tag{18}$$

To realize $\langle \hat{\eta}(t) \rangle_Q$ as an effective c-number noise, following Ray and co-workers [28,29] we now introduce the ansatz that the momenta $\langle \hat{p}_j(0) \rangle_Q$ and the shifted coordinate $[\langle \hat{x}_j(0) \rangle_Q - c_j \langle \hat{q}(0) \rangle_Q]$ of the bath oscillators are distributed according to the canonical distribution of Gaussian form

$$P_j = N \exp\left(- \frac{\langle \hat{p}_j(0) \rangle_Q^2 + \omega_j^2 [\langle \hat{x}_j(0) \rangle_Q - c_j \langle \hat{q}(0) \rangle_Q]^2}{2\hbar\omega_j \left[\bar{n}_j(\omega_j) + \frac{1}{2} \right]} \right). \tag{19}$$

Ansatz (19) is a canonical thermal Wigner distribution function for a shifted harmonic oscillator that can be obtained as an exact solution of Wigner equation [55] for a harmonic oscillator and is always a positive-definite function. The merit of using such a distribution is that it retains its property of a pure state nonsingular distribution even at $T=0$. However, in the present work we deal with situations far from the low-temperature regime. Additionally, the distribution of the quantum-mechanical mean values of the bath oscillators reduces to the classical Maxwell-Boltzmann distribution in the thermal limit. This also gives us the flexibility to avoid operator ordering as in Eqs. (9) and (10) to derive the noise properties of the bath oscillators.

Thus, for any quantum-mechanical mean value of operator $\langle \hat{O} \rangle_Q$ which is a function of bath variables, its statistical average $\langle \cdots \rangle_S$ is

$$\langle \langle \hat{O} \rangle_Q \rangle_S = \int [\langle \hat{O} \rangle_Q P_j d\{\omega_j^2 [\langle \hat{x}_j(0) \rangle_Q - c_j \langle \hat{q}(0) \rangle_Q]\} d\langle \hat{p}_j(0) \rangle_Q]. \tag{20}$$

In Eq. (19) $\bar{n}_j(\omega_j)$ is the average thermal photon number of the jth bath oscillator at temperature T and is given by

$$\bar{n}_j(\omega_j) = \left[\exp\left(\frac{\hbar\omega_j}{k_B T} \right) - 1 \right]^{-1}. \tag{21}$$

The distribution P_j given in Eq. (19) and the definition of statistical average imply that the c-number noise $\langle \hat{\eta}(t) \rangle_Q$ given by Eq. (18) must satisfy

$$\langle \langle \hat{\eta}(t) \rangle_Q \rangle_S = 0, \tag{22}$$

$$\langle \langle \hat{\eta}(t) \hat{\eta}(t') \rangle_Q \rangle_S = \frac{1}{2} \sum_{j=1}^{N} c_j^2 \omega_j^2 \hbar\omega_j \coth\left(\frac{\hbar\omega_j}{2k_B T} \right) \cos \omega_j (t-t'). \tag{23}$$

To complete the identification of Eqs. (16) and (17) as a generalized Langevin equation, we must establish the conditions on the coupling coefficients on the bath frequencies and on the number N of bath oscillators that will ensure that $\gamma(t)$ is indeed dissipative and $\phi(t)$ is genuinely finite. A sufficient condition for $\gamma(t)$ to be dissipative is that it is positive definite and that it decreases monotonically with time. These conditions are achieved if $N \to \infty$, and if $c_j^2 \omega_j^2$, $c_j \omega_j \kappa_j$ and ω_j are sufficiently smooth functions of j [19]. As $N \to \infty$, one replaces the sum in Eqs. (6) and (7) by integrals over ω, weighted by the density of states $\rho(\omega)$ and multiplied by the coupling functions $c(\omega)$ and $\kappa(\omega)$. The aforesaid conditions may be achieved in a variety of ways [56], one of the established choices being the following [57]. Thus, to obtain a finite result in the continuum limit, the coupling functions $c_j = c(\omega)$ and $\kappa_j = \kappa(\omega)$ are chosen as $c(\omega) = c_0 / (\omega\sqrt{\tau_c})$ and $\kappa(\omega) = \kappa_0 \omega \sqrt{\tau_c}$, respectively. Consequently, $\gamma(t)$ and $\varphi(t)$ reduce to the following form:

$$\gamma(t) = \frac{c_0^2}{\tau_c} \int_0^\infty d\omega \rho(\omega) \cos \omega t \tag{24}$$

and

$$\varphi(t) = c_0 \kappa_0 \int_0^\infty d\omega \omega \rho(\omega) \sin \omega t, \tag{25}$$

where c_0 and κ_0 are constants and $\omega_c = 1/\tau_c$ is the cutoff frequency of the bath oscillators. τ_c may be regarded as the correlation time of the bath and $\rho(\omega)$ is the density of modes of the heat bath which is assumed to be Lorentzian,

$$\rho(\omega) = \frac{2}{\pi} \frac{1}{\tau_c(\omega^2 + \tau_c^{-2})}. \tag{26}$$

The assumptions just stated above are very much akin to those of the hydrodynamical modes in a macroscopic system [58]. With these forms of $\rho(\omega)$, $c(\omega)$, $\kappa(\omega)$, $\gamma(t)$ and $\varphi(t)$ take the following forms:

$$\gamma(t) = \frac{c_0^2}{\tau_c}\exp\left(-\frac{t}{\tau_c}\right) = \frac{\Gamma}{\tau_c}\exp\left(-\frac{t}{\tau_c}\right) \tag{27}$$

and

$$\varphi(t) = \frac{c_0\kappa_0}{\tau_c}\exp\left(-\frac{t}{\tau_c}\right), \tag{28}$$

with $\Gamma=c_0^2$. For $\tau_c \to 0$, Eqs. (27) and (28) are reduced to $\gamma(t)=2\Gamma\delta(t)$ and $\varphi(t)=2c_0\kappa_0\delta(t)$, respectively. The noise correlation function [Eq. (23)] becomes

$$\langle\langle\hat{\eta}(t)\hat{\eta}(t')\rangle_Q\rangle_S = \frac{1}{2}\frac{\Gamma}{\tau_c}\int_0^\infty d\omega\hbar\omega \coth\left(\frac{\hbar\omega}{2k_BT}\right) \times \cos \omega(t-t')\rho(\omega). \tag{29}$$

At this juncture, it is important to note that p_j given by Eq. (19) is a canonical Wigner distribution for a displaced harmonic oscillator which always remains positive and contains the quantum information of the bath. A special advantage of using this distribution function is that it remains valid as a pure state nonsingular distribution even at $T=0$. Now, adding $V'(\langle\hat{q}\rangle_Q)$ on both sides of Eq. (17) we get the dynamical equation for the system variable as

$$\ddot{q}(t) + \int_0^t dt'\, \gamma(t-t')\dot{q}(t') + V'(q) = \eta(t) + \pi(t) + Q_V, \tag{30}$$

with

$$Q_V = V(q) - \langle V(\hat{q})\rangle. \tag{31}$$

Here, we have written $q=\langle\hat{q}\rangle_Q$ and $p=\langle\hat{p}\rangle_Q$ for brevity and $\eta(t)=\langle\hat{\eta}(t)\rangle_Q$ is a classical-like noise term. Now, one can identify Eq. (30) as a c-number generalized quantum Langevin equation for an open system where the bath instead of being at thermal equilibrium is modulated by an external noise $\epsilon(t)$. The quantum Langevin equation is guided by the c-number quantum noise $\eta(t)$ and a dressed classical noise $\pi(t)$. Using Eqs. (24) and (25), we obtain

$$\frac{d\gamma(t)}{dt} = -\frac{c_0}{\kappa_0}\frac{1}{\tau_c}\varphi(t). \tag{32}$$

Equation (32) expresses how the dissipative kernel $\gamma(t)$ depends on the response function $\varphi(t)$ of the medium due to the external noise $\epsilon(t)$. Since both the dissipation and the response function depend critically on the properties of the reservoir, and especially on its density of modes and its coupling to the system and the external noise source, such a relation for an open system can be anticipated intuitively. In the succeeding discussions we will concern ourselves with the consequences of this relation [see Eq. (52)] in light of the Langevin description in Sec. III and the imminent numerical analysis of the full model potential.

III. QUANTUM CORRECTION TERMS

Referring to the quantum nature of the system in the Heisenberg picture, we now write the system operators as

$$\hat{q} = q + \delta\hat{q},$$

$$\hat{p} = p + \delta\hat{p}, \tag{33}$$

where q and p are the quantum-mechanical mean values and $\delta\hat{q}$ and $\delta\hat{p}$ are the operators, and they are quantum fluctuations around their respective mean values. By construction, $\langle\delta\hat{q}\rangle_Q=\langle\delta\hat{p}\rangle_Q=0$ and they also follow the usual commutation relation $[\delta\hat{q},\delta\hat{p}]=i\hbar$. Using Eq. (33) and a Taylor-series expansion around q, one obtains

$$Q_V(q,t) = -\sum_{n\geq 2}\frac{1}{n!}V^{(n+1)}(q)\langle\delta\hat{q}^n\rangle_Q, \tag{34}$$

where $V^{(n+1)}(q)$ is the $(n+1)^{\text{th}}$ derivative of the potential $V(q)$. The calculation of $Q_V(q,t)$ depends on quantum correction factor $\langle\delta\hat{q}^n\rangle$ which may be obtained by solving the quantum corrections. Setting Eq. (33) in Eq. (4) one can easily show that the quantum correction is given by

$$\delta\ddot{\hat{q}}(t) + \int_0^t dt'\,\gamma(t-t')\,\delta\dot{\hat{q}}(t') + V''(q)\,\delta\hat{q}(t) + \sum_{n\geq 2}\frac{1}{n!}V^{n+1}(q) \times\langle\delta\hat{q}^n(t)\rangle = \delta\hat{\eta}(t), \tag{35}$$

where $\delta\hat{\eta}(t)=\hat{\eta}(t)-\eta(t)$.

We now consider that the system is confined in a harmonic potential, i.e., $V(q)=\frac{1}{2}\Omega_0^2q^2$, where Ω_0 is the frequency of the harmonic oscillator. Consequently, Eq. (35) becomes

$$\delta\ddot{\hat{q}} + \int_0^t dt'\,\gamma(t-t')\,\delta\dot{\hat{q}}(t') + \Omega_0^2\delta\hat{q}(t) = \delta\hat{\eta}(t). \tag{36}$$

The solution of Eq. (36) is

$$\delta\hat{q}(t) = h_1(t)\,\delta\hat{q}(0) + h_2(t)\,\delta\dot{\hat{q}}(0) + \int_0^t dt'\,h_2(t-t')\,\delta\hat{\eta}(t'), \tag{37}$$

where $h_1(t)$ and $h_2(t)$ are the Laplace transformations of $\tilde{h}_1(s)$ and $\tilde{h}_2(s)$, respectively, where

$$\tilde{h}_1(s) = \frac{s+\tilde{\gamma}(s)}{s^2+s\tilde{\gamma}(s)+\Omega_0^2}, \tag{38}$$

$$\tilde{h}_2(s) = \frac{1}{s^2+s\tilde{\gamma}(s)+\Omega_0^2}, \tag{39}$$

$$\text{with} \quad \tilde{\gamma}(s) = \int_0^\infty \gamma(t)\exp(-st)dt \tag{40}$$

being the Laplace transformation of the frictional kernel $\gamma(t)$. Squaring Eq. (37) and taking the quantum statistical average, we obtain

$$\begin{aligned}\langle\langle \delta\hat{q}^2(t)\rangle_Q\rangle_S &= h_1^2(t)\langle\langle \delta\hat{q}^2(0)\rangle_Q\rangle_S + h_2^2(t)\langle\langle \delta\hat{p}^2(0)\rangle_Q\rangle_S \\ &+ h_1(t)h_2(t)\langle\langle[\delta\hat{q}(0)\delta\hat{p}(0) + \delta\hat{p}(0)\delta\hat{q}(0)]\rangle_Q\rangle_S \\ &+ 2\int_0^t dt' \int_0^{t'} dt'' h_2(t-t')h_2(t-t'') \\ &\times\langle\langle \delta\hat{\eta}(t')\delta\hat{\eta}(t'')\rangle_Q\rangle_S. \end{aligned} \tag{41}$$

A standard choice of initial conditions corresponding to minimum uncertainty state is

$$\langle \delta\hat{q}^2(0)\rangle_Q = \frac{\hbar}{2\Omega_0}, \quad \langle \delta\hat{p}^2(0)\rangle_Q = \frac{\hbar\Omega_0}{2},$$

$$\langle \delta\hat{q}(0)\delta\hat{p}(0) + \delta\hat{p}(0)\delta\hat{q}(0)\rangle_Q = \hbar. \tag{42}$$

From the definitions of $h_1(t)$ and $h_2(t)$, we have

$$h_1(t) = \frac{1}{2\pi i}\int_{\epsilon-i\infty}^{\epsilon+i\infty} \tilde{h}_1(s)\exp(st)ds, \tag{43}$$

$$h_2(t) = \frac{1}{2\pi i}\int_{\epsilon-i\infty}^{\epsilon+i\infty} \tilde{h}_2(s)\exp(st)ds. \tag{44}$$

Using the residue theorem, one can easily show that for an Ohmic dissipative bath, which leads to $\gamma(t)=2\Gamma\delta(t)$, and in the underdamped region $(\Omega_0>\Gamma)$

$$h_1(t) = \exp(-\Gamma t)\left[\cos\omega_1 t + \frac{\Gamma}{\omega_1}\sin\omega_1 t\right], \tag{45}$$

$$h_2(t) = \exp(-\Gamma t)\frac{1}{\omega_1}\sin\omega_1 t, \tag{46}$$

where $\omega_1 = \pm\sqrt{\Omega_0^2-\Gamma^2}$. Now for the Ohmic dissipative bath, the double integral in Eq. (41) can be written as

$$\begin{aligned}&2\int_0^t dt' \int_0^{t'} dt'' h_2(t-t')h_2(t-t'')\langle\langle \delta\hat{\eta}(t')\delta\hat{\eta}(t'')\rangle_Q\rangle_S \\ &= \frac{2\Gamma}{\pi}\int_0^\infty d\omega\left[\hbar\omega\coth\left(\frac{\hbar\omega}{2k_BT}\right)\int_0^t dt'\int_0^{t'} dt''\right. \\ &\times\exp[-\Gamma(t-t')]\frac{\sin\omega_1(t-t')}{\omega_1} \\ &\left.\times\exp[-\Gamma(t-t')]\frac{\sin\omega(t-t'')}{\omega_1}\cos\omega(t'-t'')\right] \\ &= \frac{2\Gamma}{\pi}\int_0^\infty d\omega\hbar\omega\coth\left(\frac{\hbar\omega}{2k_BT}\right) \\ &\times\left|\frac{1-e^{(-\Gamma-i\omega)t}\left[\cos\omega_1 t + (\Gamma-i\omega)\frac{\sin\omega_1 t}{\omega_1}\right]}{\omega^2-\Omega_0^2+2i\Gamma\omega}\right|^2, \end{aligned} \tag{47}$$

where we have used Eq. (29) for quantum statistical average of two-time correlation function of quantum fluctuation term $\delta\hat{\eta}(t)$ and Eq. (26) for density of modes and $\tau_c\to 0$ for the Ohmic dissipative bath. From Eq. (47), we observe that the time dependence of the mean fluctuations in displacement is complicated, but it is reduced to a simple form for the time, which is large compared to (Γ^{-1}) and is given by

$$\langle \delta\hat{q}^2\rangle_{eq} = \frac{2\Gamma}{\pi}\int_0^\infty d\omega\left[\hbar\omega\coth\left(\frac{\hbar\omega}{2k_BT}\right)\frac{1}{(\omega^2-\Omega_0^2)^2+4\Gamma^2\omega^2}\right]. \tag{48}$$

In the weak damping regime $(\omega>\Gamma)$, one thus obtains Eq. (49) from Eq. (48),

$$\langle \delta\hat{q}^2\rangle_{eq} = \frac{\hbar}{2\Omega_0}\coth\left(\frac{\hbar\Omega_0}{2k_BT}\right). \tag{49}$$

In the classical limit, when $k_BT \gg \hbar\Omega_0$, the above expression reduces to

$$\langle \delta\hat{q}^2\rangle_{eq} = \frac{k_BT}{\Omega_0^2},$$

which is the classical equipartition theorem.

IV. QUANTUM FOKKER-PLANCK EQUATION

The classical Kramers' equation forms the dynamical basis of our understanding of noise-induced escape rate from a metastable state. It is interesting to note that although classical Kramers' equation was proposed more than 60 years ago, hopeful developments have been recently reported in the direction of quantum-mechanical analog of Kramers' problem. Quantum Kramers' theory of activated rate processes was developed primarily within a path-integral framework. The validity of the major results is restricted to activated tunneling regime. The formation of the quantum Langevin equation as developed in the earlier section is now extended to formulate a generalized quantum Kramers' equation which is valid in the deep tunneling as well as in the non-Markovian regime of a thermodynamically open system. We consider Eq. (30) and rewrite $V(q)$ as a sum of linear and nonlinear terms by expanding it in a Taylor series, say, around the bottom of the harmonic well at $q=0$ as

$$V(q) = V(0) + \tfrac{1}{2}\Omega_0^2 q^2 + V_N(q), \tag{50}$$

where $V_N(q)$ is the total nonlinear contribution and Ω_0^2 refers to $V''(0)$. With the help of Eq. (50), the Langevin equation may be rewritten as

$$\ddot{q} + \Omega_0^2 q + \int_0^t dt'\gamma(t-t')\dot{q}(t') = -V_N'(q) + Q_V + \eta(t) + \pi(t). \tag{51}$$

The two potential dependent terms on the right-hand side of Eq. (51) can be evaluated as a function of time t so that we may treat the entire right-hand side including noise terms $\xi(t)=\eta(t)+\pi(t)$ as an inhomogeneous contribution. We therefore write

$$\ddot{q}+\Omega_0^2 q+\int_0^t dt'\,\gamma(t-t')\dot{q}(t')=Q_T(t)+\eta(t)+\pi(t),$$

$$\text{or}\quad \ddot{q}=-\Omega_0^2 q-\int_0^t dt'\,\gamma(t-t')\dot{q}(t')+Q_T(t)+\eta(t)-\int_0^t dt'\,\varphi(t-t')\epsilon(t'), \tag{52}$$

where $Q_T=Q_V-V_N'$. The Laplace transform of Eq. (52) allows us to write a formal solution for the displacement of the form

$$q(t)=\langle q(t)\rangle_s+\int_0^t dt' H(t-t')\eta(t')-\frac{\kappa_0}{c_0}\tau_c\Omega_0^2\int_0^t dt' H(t-t')\epsilon(t')-\frac{\kappa_0}{c_0}\tau_c\int_0^t dt' H_2(t-t')\epsilon(t'), \tag{53}$$

where we have made use of relation (32) explicitly. Here,

$$\langle q(t)\rangle=\chi_q(t)q(0)+H(t)\dot{q}(0)+G(t), \tag{54}$$

$$G(t)=\int_0^t dt' H(t-t')Q_T(t'), \tag{55}$$

with $q(0)$ and $\dot{q}(0)$ being the initial position and initial velocity of the oscillator, respectively, which are nonrandom and

$$\chi_q(t)=1-\Omega_0^2\int_0^t H(t')dt'. \tag{56}$$

The kernel $H(t)$ is the Laplace inversion of

$$\tilde{H}(s)=\frac{1}{s^2+\tilde{\gamma}(s)s+\Omega_0^2}, \tag{57}$$

where $\tilde{\gamma}(s)=\int_0^\infty \exp(-st)\gamma(t)dt$ is the Laplace transform of the friction kernel $\gamma(t)$ and

$$H_2(t)=\frac{d^2H(t)}{dt^2}. \tag{58}$$

The time derivative of Eq. (53) yields

$$\dot{q}(t)=\langle \dot{q}(t)\rangle_S+\int_0^t dt' H_1(t-t')\eta(t')-\frac{\kappa_0}{c_0}\tau_c\Omega_0^2\int_0^t dt' H_1(t-t')\epsilon(t')-\frac{\kappa_0}{c_0}\tau_c\int_0^t dt' H_3(t-t')\epsilon(t'), \tag{59}$$

$$\text{where}\quad \langle\dot{q}(t)\rangle_S=H_1(t)\dot{q}(0)-\Omega_0^2 H(t)q(0)+g(t), \tag{60}$$

$$\text{with}\quad g(t)=\dot{G}(t)$$

$$\text{and}\quad H_1(t)=\frac{dH}{dt},\quad H_3(t)=\frac{d^3H}{dt^3}. \tag{61}$$

Next, we calculate the variances. From the formal solution of $q(t)$ and $v(t)[=\dot{q}(t)]$, the explicit expressions for the variances are obtained, which are given below,

$$\begin{aligned}\sigma_{qq}^2(t)&=\langle[q(t)-\langle q(t)\rangle_S]^2\rangle_S=2\int_0^t dt_1 H(t_1)\int_0^{t_1} dt_2 H(t_2)\\&\times\langle\eta(t_1)\eta(t_2)\rangle+2\left(\frac{\kappa_0}{c_0}\tau_c\Omega_0^2\right)^2\int_0^t dt_1 H(t_1)\int_0^{t_1} dt_2 H(t_2)\\&\times\langle\epsilon(t_1)\epsilon(t_2)\rangle+2\left(\frac{\kappa_0}{c_0}\tau_c\right)^2\int_0^t dt_1 H_2(t_1)\int_0^{t_1} dt_2 H_2(t_2)\\&\times\langle\epsilon(t_1)\epsilon(t_2)\rangle+2\left(\frac{\kappa_0}{c_0}\tau_c\right)^2\Omega_0^2\int_0^t dt_1 H(t_1)\int_0^{t_1} dt_2 H_2(t_2)\\&\times\langle\epsilon(t_1)\epsilon(t_2)\rangle,\end{aligned} \tag{62}$$

$$\begin{aligned}\sigma_{vv}^2(t)&=\langle[v(t)-\langle v(t)\rangle_S]^2\rangle_S=2\int_0^t dt_1 H_1(t_1)\int_0^{t_1} dt_2 H_1(t_2)\\&\times\langle\eta(t_1)\eta(t_2)\rangle\\&+2\left(\frac{\kappa_0}{c_0}\tau_c\Omega_0^2\right)^2\int_0^t dt_1 H_1(t_1)\int_0^{t_1} dt_2 H_1(t_2)\langle\epsilon(t_1)\epsilon(t_2)\rangle\\&+2\left(\frac{\kappa_0}{c_0}\tau_c\right)^2\int_0^t dt_1 H_3(t_1)\int_0^{t_1} dt_2 H_3(t_2)\langle\epsilon(t_1)\epsilon(t_2)\rangle\\&+2\left(\frac{\kappa_0}{c_0}\tau_c\right)^2\Omega_0^2\int_0^t dt_1 H_1(t_1)\int_0^{t_1} dt_2 H_3(t_2)\langle\epsilon(t_1)\epsilon(t_2)\rangle,\end{aligned} \tag{63}$$

$$\text{and}\quad \sigma_{qv}^2(t)=\langle[q(t)-\langle q(t)\rangle_S][v(t)-\langle v(t)\rangle_S]\rangle_S=\tfrac{1}{2}\dot{\sigma}_{qq}^2(t), \tag{64}$$

where we have assumed that the correlation functions of the noises $\eta(t)$ and $\epsilon(t)$ are symmetric with respect to the time argument and have made use of the fact that $\eta(t)$ and $\epsilon(t)$ are uncorrelated. Having obtained the expression for the statistical averages and variances, we are now in a position to write down quantum Kramers' equation which is a Fokker-Planck description of probability density function $P(q,v,t)$ of the quantum-mechanical mean values of the coordinate and the momentum operators of the particle. Assuming the statistical description of the noise $\eta(t)$ and $\epsilon(t)$ to be Gaussian, we define the joint characteristic function $\tilde{P}(\mu,\rho,t)$ where (q,r) and (v,ρ) are the Fourier transform pair of the variables. Then, using the standard procedure, we arrive at the equation of motion for probability distribution function $P(\mu,\rho,t)$, which is the inverse Fourier transform of $\tilde{P}(\mu,\rho,t)$,

$$\frac{\partial P(q,v,t)}{\partial t} = \frac{\partial}{\partial q}[\{-v+g(t)\}P(q,v,t)] + \frac{\partial}{\partial v}[\{\tilde{V}'(q)+\Omega(t) - N(t)\}P(q,p,t)] + \frac{\partial}{\partial v}[\gamma(t)v]P(q,v,t) + \phi(t)\frac{\partial^2 P}{\partial v^2} + \psi(t)\frac{\partial^2 P}{\partial q\,\partial v}, \tag{65}$$

where

$$\gamma(t) = -\frac{\partial}{\partial t}[\ln Y(t)], \tag{66a}$$

$$Y(t) = \frac{H_1(t)}{\Omega_0^2}\left[1-\Omega_0^2\int_0^t dt' H(t')\right] + H^2(t), \tag{66b}$$

$$\tilde{\Omega}_0^2(t) = \frac{-H(t)H_1(t)+H_1^2(t)}{Y(t)}, \tag{66c}$$

$$N(t) = \frac{1}{Y(t)}\left[-\frac{1}{\Omega_0^2}g(t)H_2(t)\left\{1-\Omega_0^2\int_0^t H(t')dt'\right\} + H_1^2(t)G(t)\right], \tag{66d}$$

$$\Omega(t) = H(t)\frac{d}{dt}[G(t)H_1(t)], \tag{66e}$$

$$\phi(t) = \tilde{\Omega}_0^2(t)\sigma_{qv}^2(t) + \gamma(t)\sigma_{vv}^2(t) + \tfrac{1}{2}\dot{\sigma}_{qv}^2(t), \tag{66f}$$

$$\psi(t) = \dot{\sigma}_{qv}^2(t) + \gamma(t)\sigma_{qv}^2(t) + \tilde{\Omega}_0^2(t)\sigma_{qq}^2(t) - \sigma_{vv}^2(t), \tag{66g}$$

where $V(q)$ is the renormalized potential linearized at $q=0$, the frequency being $\tilde{\Omega}_0^2(t)$ as given in Eq. (66c). The Fokker-Planck equation [Eq. (65)] is the quantum-mechanical version of classical non-Markovian Kramers' equation for an open system and is valid for arbitrary temperature and friction. It is interesting to note that due to its explicit dependence on $Q(t)$, the quantities $g(t)$, $\Omega(t)$, and $N(t)$ manifestly include quantum effects through the nonlinearity of the system potential. In classical limit, $(k_BT \gg \hbar\Omega_0)$, $\phi(t)$ and $\psi(t)$ can be obtained by applying classical fluctuation-dissipation relation in Eqs. (66f) and (66g).

To proceed further it is worth noting that the classical-like stochastic differential equation [Eq. (52)], and hence, the generalized quantum Fokker-Planck equation [Eq. (65)] contain essential quantum features through the term $\eta(t)$ which represents the quantum noise of the heat bath and another term Q_V which essentially arises due to the nonlinear part of the potential. The $\epsilon(t)$-containing term in Eq. (52) represents the fact that the bath is modulated by an external noise and consequently the system is acted upon by an effective noise,

$$\pi(t) = -\int_0^t dt'\,\varphi(t-t')\epsilon(t').$$

At this point it is interesting to note the form of Eq. (65) for a harmonic potential, for which $Q_T(t)=0$. In this case, Eq. (65) reduces to the form

$$\frac{\partial P}{\partial t} = -v\frac{\partial p}{\partial q} + \tilde{\Omega}_0^2(t)q\frac{\partial P}{\partial v} + \lambda(t)\frac{\partial}{\partial v}(vP) + \phi(t)\frac{\partial^2 P}{\partial v^2} + \psi(t)\frac{\partial^2 P}{\partial q\,\partial v}. \tag{67}$$

We now discuss the asymptotic properties of $\phi(t)$ and $\psi(t)$ which in turn are dependent on the variances $\sigma_{qq}^2(t)$ and $\sigma_{vv}^2(t)$ as $t\to\infty$ since they play a significant role in our further analysis that follows. From Eqs. (62) and (63) we may write

$$\sigma_{qq}^2(t) = \sigma_{qq}^{2(i)}(t) + \sigma_{qq}^{2(e)}(t)$$

$$\text{and}\quad \sigma_{vv}^2(t) = \sigma_{vv}^{2(i)}(t) + \sigma_{vv}^{2(e)}(t),$$

where i denotes the part that corresponds to the internal noise $\eta(t)$ and e corresponds to external noise $\epsilon(t)$. Since the average velocity of the oscillator is 0, as $t\to\infty$, we see from Eq. (60) [with $g(t)=0$ for harmonic oscillator] that $H(t)$ and $H_1(t)$ must be 0 as $t\to\infty$. Also, from Eq. (54) [with $G(t)=0$ for harmonic oscillator] we observe that the function $\chi_q(t)$ must decay to zero for long time. Hence, from Eq. (56) we see that the stationary value of the integral of $H(t)$ is $1/\Omega_0^2$, i.e.,

$$\int_0^\infty H(t)dt = \frac{1}{\Omega_0^2}. \tag{68}$$

Now for harmonic oscillator, $\sigma_{qq}^{2(i)}(t)$ and $\sigma_{vv}^{2(i)}(t)$ of Eqs. (62) and (63) can be written in the form [see Eq. (49)]

$$\sigma_{qq}^{2(i)}(t) = 2\int_0^t dt_1 H(t_1)\int_0^{t_1} dt_2 H(t_2)\langle\eta(t_1)\eta(t_2)\rangle = \frac{\hbar\Omega_0}{2}\coth\left(\frac{\hbar\Omega_0}{2k_BT}\right)\left[2\int_0^t dt' H(t') - H^2(t) - \Omega_0^2\left(\int_0^t dt' H(t')\right)^2\right] \tag{69}$$

$$\text{and}\quad \sigma_{vv}^{2(i)}(t) = 2\int_0^t dt_1 H_1(t_1)\int_0^{t_1} dt_2 H_1(t_2)\langle\eta(t_1)\eta(t_2)\rangle = \frac{1}{2}\hbar\Omega_0\coth\left(\frac{\hbar\Omega_0}{2k_BT}\right)[1-H_1^2(t)-\Omega_0^2H^2(t)]. \tag{70}$$

From the above two expressions [Eqs. (69) and (70)], we see that

$$\sigma_{qq}^{2(i)}(\infty) = \frac{\hbar}{2\Omega_0}\coth\left(\frac{\hbar\Omega_0}{2k_BT}\right), \tag{71}$$

$$\sigma_{vv}^{2(i)}(\infty) = \frac{1}{2}\hbar\Omega_0 \coth\left(\frac{\hbar\Omega_0}{2k_BT}\right). \tag{72}$$

The classical limit of Eq. (71) is $\sigma_{qq}^{2(i)}(\infty)=k_BT/\Omega_0^2$ ($k_BT \gg \hbar\Omega_0$), which is the classical equipartition of energy, and the classical limit of Eq. (72) is $\sigma_{vv}^{2(i)}(\infty)=k_BT$. It is important to note that these stationary values are not related to the intensity and correlation time of the external noise.

We next consider the parts $\sigma_{qq}^{2(e)}(t)$ and $\sigma_{vv}^{2(e)}(t)$ due to the presence of external noise. The Laplace transform of Eq. (53) yields the expression

$$\tilde{q}(s) - \langle\tilde{q}(s)\rangle_S = \tilde{H}(s)\tilde{\eta}(s) - \frac{\kappa_0}{c_0}\tau_c\Omega_0^2\tilde{H}(s)\tilde{\epsilon}(s) - \frac{\kappa_0}{c_0}\tau_c s^2\tilde{H}(s)\tilde{\epsilon}(s), \tag{73}$$

where

$$\langle\tilde{q}(s)\rangle_S = \left\{\frac{1}{s} - \Omega_0^2\frac{\tilde{H}(s)}{s}\right\}q(0) + \tilde{H}(s)\dot{q}(0). \tag{74}$$

From the above equation [Eq. (73)], we can calculate the variance σ_{qq}^2 in the Laplace transformed space which can be identified as the Laplace transform of Eq. (62). Thus, for the part $\sigma_{qq}^{2(e)}$, we observe that $\sigma_{qq}^{2(e)}(s)$ contains terms like $[(\kappa_0/c_0)\tau_c\Omega_0^2\tilde{H}(s)]^2\langle\tilde{\epsilon}^2(s)\rangle$. Since we have assumed the stationarity of the noise $\epsilon(t)$, we conclude that if $\tilde{c}(0)$ exists [where $c(t-t')=\langle\epsilon(t)\epsilon(t')\rangle$], then the stationary value of $\sigma_{qq}^{2(e)}(t)$ exists and becomes a constant that depends on the correlation time and the strength of the noise. Similar argument is also valid for $\sigma_{vv}^{2(e)}(t)$. Now summarizing the above discussion, we note that (i) the internal noise-driven parts $\sigma_{qq}^2(t)$ and $\sigma_{vv}^2(t)$, that is, $\sigma_{qq}^{2(i)}(t)$ and $\sigma_{vv}^{2(i)}(t)$, approach the fixed values which are independent of the noise correlation and intensity at $t\to\infty$ and (ii) the external noise-driven parts of the variances also approach the constant values at the stationary limit ($t\to\infty$) which are dependent on the strength and the correlation time of the noise. Hence, we conclude that even in the presence of an external noise, the coefficients of the Fokker-Planck equation [Eq. (67)] do exist asymptotically and we write its steady-state version for the asymptotic values of the parameters as

$$-v\frac{\partial P}{\partial q} + \tilde{\Omega}_0^2 q\frac{\partial P}{\partial v} + \gamma\frac{\partial}{\partial v}(vP) + \phi(\infty)\frac{\partial^2 P}{\partial v^2} + \psi(\infty)\frac{\partial^2 P}{\partial q\,\partial v} = 0, \tag{75}$$

where γ, Ω_0^2, $\phi(\infty)$, and $\psi(\infty)$ are to be evaluated from the general definition [Eqs. (66a), (66c), (66f), and (66g)], respectively, for the steady state.

The general steady-state solution of the above equation [Eq. (75)] is

$$P_{st}(q,v) = \frac{1}{Z}\exp\left[-\left\{\frac{v^2}{2D_0} + \frac{\tilde{\Omega}_0^2 q^2}{2(D_0+\psi(\infty))}\right\}\right], \tag{76}$$

$$\text{where}\quad D_0 = \frac{\phi(\infty)}{\gamma} \tag{77}$$

and Z is the normalization constant. The solution [Eq. (76)] can be verified by direct substitution. The distribution [Eq. (76)] is not an equilibrium distribution. This stationary distribution for the nonequilibrium open system plays the role of an equilibrium distribution of the closed system which may, however, be recovered in the absence of any external noise term.

Some further pertinent points regarding the rate theory for nonequilibrium systems may be put in order. It is well known that the equilibrium state of a closed thermodynamic system with homogeneous boundary conditions is time independent. The open, that is, the driven system, on the contrary, may demonstrate complicated spatiotemporal structures or may settle down to multiple steady states. The external noise may then include transitions between them. It is, however, important to realize that these features originate only when one takes into account the nonlinearity of the system in full, and the external noise drives the system directly. Second, in most of the open nonequilibrium systems, the lack of detailed balance symmetry gives rise to several problems in the determination of the stationary probability distribution for multidimensional problems. At this juncture, three points are to be noted. First, for the present problem, we have made use of the linearization of the potential at the bottom and at the top of the barrier (as is done in Kramers' development [12] and in most of the post-Kramers' one [1]) which precludes existence of the multiple steady states. Second, the external noise considered here drives the bath rather than the system directly. Lastly, the problem is one dimension. Thus, a unique stationary probability density, which is an essential requirement for the mean fast passage time of flux over population method (as in the present case) for the calculation of rate and which is readily obtainable in the case of closed nonequilibrium system, can also be obtained for this open nonequilibrium quantum system.

V. KRAMERS' ESCAPE RATE

We now turn to the problem of decay of a metastable state. To this end we consider as usual a Brownian particle moving in a one-dimensional double-well potential $V(q)$. In Kramers' approach [1], the particle coordinate q corresponds to the reaction coordinate and its values at the minimum of the potential $V(q)$ denote the reactant and product states. The maximum of $V(q)$ at q_b separating these states corresponds to the activated complex. All the remaining degrees of freedom of both the reactant and solvent constitute a heat bath at a temperature T. Our object is to calculate the essential modification of Kramers' rate in the semiclassical regime when the bath modes are perturbed by an external random force under the condition that the system has attained a steady state.

Linearizing the motion around the barrier top at $q=q_b$, the Langevin equation [Eq. (52)] can be written as

$$\dot{y} = v,$$

$$\dot{v} = \Omega_b^2 y - \int_0^t dt' \gamma(t-t') v(t') + \eta(t) + \pi(t), \qquad (78)$$

where $y=q-q_b$ and the barrier frequency Ω_b^2 is defined by

$$V(y) = V_b - \tfrac{1}{2}\Omega_b^2 y^2, \quad \Omega_b^2 > 0. \qquad (79)$$

Correspondingly, the motion of the particle is governed by the Fokker-Planck equation [Eq. (67)],

$$\frac{\partial P}{\partial t} = -v\frac{\partial p}{\partial y} - \tilde{\Omega}_b^2(t) y \frac{\partial P}{\partial v} + \gamma_b(t)\frac{\partial}{\partial v}(vP) + \phi_b(t)\frac{\partial^2 P}{\partial v^2} + \psi_b(t)\frac{\partial^2 P}{\partial y\,\partial v}, \qquad (80)$$

where the subscript b indicates that all the coefficients are to be calculated using the general definition [Eqs. (66a)–(66g)] for the barrier top region.

It is apparent from Eqs. (75) and (80) that since the dynamics is non-Markovian and the system is thermodynamically open, one has to deal with the renormalized frequencies $\tilde{\Omega}_0$ and $\tilde{\Omega}_b$ near the bottom and the top of the well, respectively. Following Kramers' [1], we make the ansatz that the nonequilibrium steady-state probability, P_b, generating a nonvanishing diffusion current j across the barrier, is given by

$$P_b(q,v) = \exp\left[-\left\{\frac{v^2}{2D_b} + \frac{\tilde{V}(q)}{D_b + \psi_b(\infty)}\right\}\right] F(q,v), \qquad (81)$$

$$\text{where} \quad D_b = \frac{\phi_b(\infty)}{\gamma_b} \qquad (82)$$

and $\tilde{V}(q)$ is the renormalized linear potential expressed as

$$\tilde{V}(q) = V(q_0) + \tfrac{1}{2}\tilde{\Omega}_0^2(q-q_0)^2, \quad \text{near the bottom},$$

$$\tilde{V}(q) = V(q_b) - \tfrac{1}{2}\tilde{\Omega}_b^2(q-q_b)^2, \quad \text{near the top}, \qquad (83)$$

with $\tilde{\Omega}_0^2, \tilde{\Omega}_b^2 > 0$. The unknown function, $F(q,v)$, obeys the general boundary condition that for $q \to \infty$, $F(q,v)$ vanishes.

The form of the ansatz in Eq. (81), denoting the steady-state distribution, is motivated by the local analysis near the bottom and the top of the barrier in Kramers' sense [1]. For a stationary nonequilibrium system on the other hand, the relative population of the two regions, in general, depends on the global properties of the potential, leading to an additional factor in the rate expression. Although, Kramers' type ansatz [1], which is valid for the local analysis, such a consideration is outside the scope of the present treatment, we point out a distinctive feature in the ansatz given in Eq. (81) vis-à-vis Kramers' ansatz [1]. While in the latter case one considers a complete factorization of the equilibrium (Boltzmann) and the dynamical parts, the ansatz in Eq. (81), on the contrary, incorporates the additional dynamical contribution through dissipation and strength of the noise into the exponential part. This modification of Kramers' ansatz (by dynamics) is due to the nonequilibrium nature of the system. Thus, unlike Kramers, the exponential factor in Eq. (81) and the stationary distribution in Eq. (76), which serve the purpose of a boundary condition, are characteristically different. While a global analysis may even modify the standard Kramers' result, our aim here is to understand the modification of the rate due to the modulation of the bath driven by an external noise in the semiclassical regime but within the purview of Kramers' type ansatz. The internal consistency of the treatment, however, can be checked by recovering the standard Kramers' result when the external noise is switched off (in the classical regime).

From Eq. (80), using Eq. (81), we obtain the equation for $F(y,v)$ in the steady state in the neighborhood of q_b as

$$-\left(1 + \frac{\psi_b(\infty)}{D_b}\right) v \frac{\partial F}{\partial y} - \left[\frac{D_b}{D_b + \psi_b(\infty)}\tilde{\Omega}_b^2 y + \gamma_b v\right]\frac{\partial F}{\partial v} + \phi_b(\infty)\frac{\partial^2 F}{\partial v^2} + \psi_b(\infty)\frac{\partial^2 F}{\partial v\,\partial y} = 0. \qquad (84)$$

We then make use of the transformation, $u=v+ay, y=q-q_b$, where a is a constant to be determined, obtained from Eq. (84),

$$\{\phi_b(\infty) + a\psi_b(\infty)\}\frac{d^2F}{du^2} - \left[\frac{D_b}{D_b + \psi_b(\infty)}\tilde{\Omega}_b^2 y + \left\{\gamma_b + a\left(1 + \frac{\psi_b(\infty)}{D_b}\right)\right\} v\right]\frac{dF}{du} = 0. \qquad (85)$$

Substituting

$$\frac{D_b}{D_b + \psi_b(\infty)}\tilde{\Omega}_b^2 y + \left\{\gamma_b + a\left(1 + \frac{\psi_b(\infty)}{D_b}\right)\right\} v = -\beta u \qquad (86)$$

(with β being another constant to be determined), we obtain the ordinary differential equation for $F(u)$,

$$\frac{d^2F}{dv^2} + \Lambda u \frac{dF}{du} = 0, \qquad (87)$$

$$\text{where} \quad \Lambda = \frac{\beta}{\phi_b(\infty) + a\psi_b(\infty)} \qquad (88)$$

and the two constants β and a must satisfy the simultaneous relation

$$-\beta a = \frac{D_b}{D_b + \psi_b(\infty)}\tilde{\Omega}_b^2, \qquad (89)$$

$$-\beta = \gamma_b + a\left(1 + \frac{\psi_b(\infty)}{D_b}\right). \qquad (90)$$

This implies that the constant a must satisfy the quadratic equation

$$\frac{D_b + \psi_b(\infty)}{D_b} a^2 + \gamma_b a - \frac{D_b}{D_b + \psi_b(\infty)}\tilde{\Omega}_b^2 = 0, \qquad (91)$$

which allows

$$a_\pm = \frac{D_b}{2[D_b + \psi_b(\infty)]}\left(-\gamma_b \pm \sqrt{\gamma_b^2 + 4\tilde{\Omega}_b^2}\right). \qquad (92)$$

The general solution of Eq. (87) is

$$F(u) = F_2 \int_0^u \exp\left(-\frac{\Lambda z^2}{2}\right) dz + F_1, \quad (93)$$

where F_1 and F_2 are the constants of integration. We look for a solution which vanishes for large q. For this to happen, the integral in Eq. (93) should remain finite for $|u| \to +\infty$. This implies that $\Lambda > 0$, so that only a_- becomes relevant. The requirement $P_b(q,v) \to 0$ for $q \to +\infty$ yields

$$F_1 = F_2 \left(\sqrt{\frac{\pi}{2\Lambda}}\right). \quad (94)$$

Thus, we have

$$F(u) = F_2 \left[\sqrt{\frac{\pi}{2\Lambda}} + \int_0^u \exp\left(-\frac{\Lambda z^2}{2}\right) dz\right] \quad (95a)$$

and correspondingly

$$P_b(q,v) = F_2 \left[\sqrt{\frac{\pi}{2\Lambda}} + \int_0^u \exp\left(-\frac{\Lambda z^2}{2}\right) dz\right] \times \exp\left[-\left\{\frac{v^2}{2D_b} + \frac{\tilde{V}(q)}{D_b + \psi_b(\infty)}\right\}\right]. \quad (95b)$$

The current across the barrier associated with this distribution is given by

$$j = \int_{-\infty}^{+\infty} v P_b(q = q_b, v) dv, \quad (96a)$$

which may be evaluated using Eq. (95b) and the linearized version of $\tilde{V}(q)$, namely, $\tilde{V}_q = V(q_b) - \frac{1}{2}\tilde{\Omega}_b^2 (q - q_b)^2$,

$$j = F_2 \left(\frac{2\pi}{\Lambda + D_b^{-1}}\right)^{1/2} D_b \exp\left[-\frac{V(q_b)}{D_b + \psi(\infty)}\right]. \quad (96b)$$

To determine the remaining constant F_2, we proceed as follows. We first note that as $q \to -\infty$, the pre-exponential factor in Eq. (95b) reduces to the following form:

$$F_2 \left[\sqrt{\frac{\pi}{2\Lambda}} + \int_0^u \exp\left(-\frac{\Lambda z^2}{2}\right) dz\right] = F_2 \left(\frac{2\pi}{\Lambda}\right)^{1/2}. \quad (97)$$

We then obtain the reduced distribution function in q as

$$\tilde{P}_b(q \to -\infty) = 2\pi F_2 \left(\frac{D_b}{\Lambda}\right)^{1/2} \exp\left[-\frac{V(q)}{D_b + \psi(\infty)}\right], \quad (98)$$

where we have used the definition for the reduced distribution as $\tilde{P}_b(q) = \int_{-\infty}^{+\infty} P(q,v) dv$. Similarly, we derive the reduced distribution in the left well around $q \approx q_0$, with a linearized potential $\tilde{V}_q = V(q_0) + \frac{1}{2}\tilde{\Omega}_0^2 (q - q_0)^2$ using Eq. (76) as

$$\tilde{P}_{st}(q) = \frac{1}{Z}\sqrt{2\pi D_0} \exp\left[-\frac{V(q_0)}{D_0 + \psi_0(\infty)}\right] \times \exp\left[-\frac{\tilde{\Omega}_0^2 (q - q_0)^2}{2(D_0 + \psi_0(\infty))}\right], \quad (99a)$$

with the normalization constant $1/Z$, where

$$\frac{1}{Z} = \frac{\tilde{\Omega}_0}{2\pi\sqrt{D_0[D_0 + \psi_0(\infty)]}} \exp\left[\frac{V(q_0)}{D_0 + \psi_0(\infty)}\right]. \quad (99b)$$

The comparison of the distributions [Eqs. (98) and (99a)] near $q = q_0$, that is, $\tilde{P}_{st}(q_0) = \tilde{P}_b(q_0)$, gives

$$F_2 = \left(\frac{\Lambda}{D_b}\right) \frac{\tilde{\Omega}_0}{2\pi\sqrt{D_0[D_0 + \psi_0(\infty)]}} \exp\left[\frac{V(q_0)}{D_0 + \psi_0(\infty)}\right]. \quad (100)$$

Hence, from Eq. (96b), the normalized current or the barrier crossing rate k is given by

$$k = \frac{\tilde{\Omega}_0}{2\pi} \frac{D_b}{\{D_0 + \psi_0(\infty)\}^{1/2}} \left(\frac{\Lambda}{1 + \Lambda D_b}\right)^{1/2} \exp\left[-\frac{E_0}{D_b + \psi_b(\infty)}\right], \quad (101)$$

where E_0 is the activation energy, $E_0 = V(q_b) - V(q_0)$. Since the temperature term due to the thermal noise, the strength of the external noise and the damping constant is buried in the parameters D_0, D_b, ψ_b, ψ_0 and Λ, the generalized expression looks somewhat cumbersome. We point out that the subscripts 0 and b in D and ψ refer to the well and the barrier top region, respectively. Equation (101) is the central result of the present work. The dependence of the rate on the parameters can be explored explicitly once we consider the limiting cases. For simplicity, we highlight the specific cases when the external noise $\epsilon(t)$ is assumed to be δ correlated, that is,

$$\langle \epsilon(t)\epsilon(t')\rangle = 2D\delta(t - t'). \quad (102)$$

In such a situation, after some lengthy, however, straightforward algebra, one gets

$$\sigma_{qq}^2(\infty) = \frac{\hbar}{2\Omega_0} \coth\left(\frac{\hbar\Omega_0}{2k_B T}\right) + \frac{D\kappa_0^2}{\Omega_0^2}, \quad (103)$$

$$\sigma_{vv}^2(\infty) = \frac{\hbar\Omega_0}{2} \coth\left(\frac{\hbar\Omega_0}{2k_B T}\right) + D\kappa_0^2, \quad (104)$$

$$\text{and} \quad \sigma_{qv}^2(\infty) = 0. \quad (105)$$

These variances yield $\phi(\infty)$, $\psi(\infty)$, and certain other relevant quantities as

$$\phi(\infty) = \gamma\left[\frac{1}{2}\hbar\Omega_0 \coth\left(\frac{\hbar\Omega_0}{2k_B T}\right) + D\kappa_0^2\right] \quad (106a)$$

$$\text{and} \quad \psi(\infty) = 0, \quad (106b)$$

which gives

$$D_0 = \frac{\phi(\infty)}{\gamma} = \frac{1}{2}\hbar\Omega_0 \coth\left(\frac{\hbar\Omega_0}{2k_B T}\right) + D\kappa_0^2. \quad (106c)$$

Hence, from Eq. (76) we see that the steady-state distribution is given by

$$\widetilde{P}_{st}(q,v) = \frac{1}{Z}\exp\left[-\frac{\Omega_0^2 q^2 + v^2}{\hbar\Omega_0 \coth\left(\frac{\hbar\Omega_0}{2k_BT}\right) + D\kappa_0^2}\right]. \tag{107}$$

In the absence of external noise ($D=0$) and in the classical regime ($k_BT \gg \hbar\Omega_0$), the above expression reduces to

$$\widetilde{P}_{st}(q,v) = \frac{1}{Z}\exp\left[-\frac{\Omega_0^2 q^2 + v^2}{2k_BT}\right], \tag{108}$$

which is the correct equilibrium distribution for a classical harmonic oscillator. In writing the above distribution function we have made use of the fact that for the Markovian process $\widetilde{\Omega}_0^2=\Omega_0^2$. From the above expression [Eq. (108)], we see that the steady-state probability distribution function does not depend on the correlation time of the thermal noise but depends clearly on the strength and the coupling of the external noise.

We now return to our generalized rate expression [Eq. (101)]. For the present case, we have

$$\psi_0(\infty) = \psi_b(\infty) = 0, \tag{109}$$

$$D_0 = \frac{1}{2}\hbar\Omega_0 \coth\left(\frac{\hbar\Omega_0}{2k_BT}\right) + D\kappa_0^2, \tag{110}$$

$$D_b = \frac{1}{2}\hbar\Omega_b \coth\left(\frac{\hbar\Omega_b}{2k_BT}\right) + D\kappa_0^2, \tag{111}$$

$$\widetilde{\Omega}_0^2 = \Omega_0^2, \quad \widetilde{\Omega}_b^2 = \Omega_b^2, \tag{112}$$

$$\Lambda = \frac{\beta}{c_0^2\left[\frac{1}{2}\hbar\Omega_0 \coth\left(\frac{\hbar\Omega_b}{2k_BT}\right) + D\kappa_0^2\right]}, \tag{113}$$

$$\text{and} \quad a_- = -\frac{c_0^2}{2} - \sqrt{\frac{c_0^4}{4} + \Omega_b^2}. \tag{114}$$

Using all these values, we obtain from Eq. (101)

$$k = \frac{\Omega_0}{2\pi\Omega_b}\left[\left\{\frac{c_0^4}{4} + \Omega_b^2\right\}^{1/2} - \frac{c_0^2}{2}\right]\left[\frac{\Omega_b \coth\frac{\hbar\Omega_b}{2k_BT} + D\kappa_0^2}{\Omega_0 \coth\frac{\hbar\Omega_b}{2k_BT} + D\kappa_0^2}\right] \times\exp\left[-\frac{E_0}{\frac{1}{2}\hbar\Omega_b \coth\left(\frac{\hbar\Omega_b}{2k_BT}\right) + D\kappa_0^2}\right]. \tag{115}$$

The high-temperature limit ($k_BT \gg \hbar\Omega_0, \hbar\Omega_b$), the above semiclassical rate [Eq. (115)], is reduced to

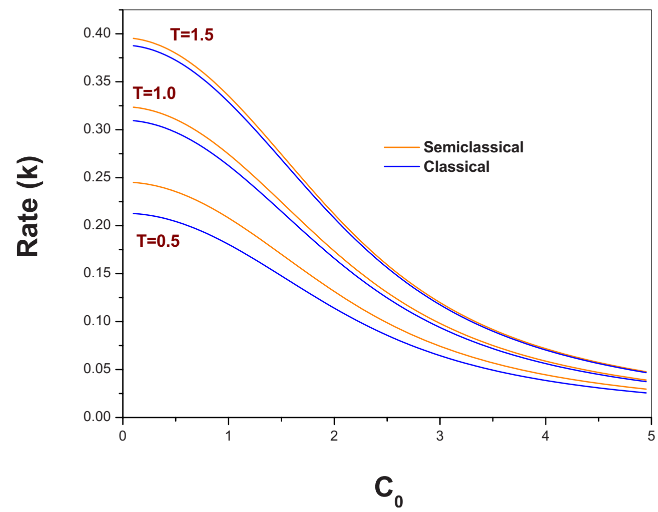

FIG. 1. (Color online) Variation of rate (k) with c_0 for different temperatures with $D=1.0$, $k_B=1.0$, $\hbar=1.0$, $k_0=1.0\Omega_0=1.0$, $E_0=2.25$, and $\Omega_b=3.0$.

$$k_{\text{classical}} = \frac{\Omega_0}{2\pi\Omega_b}\left[\left\{\frac{c_0^4}{4} + \Omega_b^2\right\}^{1/2} - \frac{c_0^2}{2}\right]\exp\left[-\frac{E_0}{2k_BT + D\kappa_0^2}\right]. \tag{116}$$

If we set the external noise intensity $D=0$, that is, when the external noise is absent, the above expression reduces to the traditional Kramers' expression with $c_0^2=\Gamma$.

Now, the semiclassical contribution (when the external noise is δ correlated) toward the escape rate is given by

$$k_{\text{semiclassical}} = k - k_{\text{classical}}. \tag{117}$$

In Sec. VI, we essentially set Eqs. (115) and (116) to rigorous numerical test and analyze the results obtained. In conclusion to this section, we point out that had we chose to work with purely Gaussian white noises (which are delta correlated) in both external driving and the internal force fields, we would have arrived at the same result as obtained by Ray Chaudhuri *et al.* in Ref. [50].

VI. RESULTS AND DISCUSSION

To illustrate the applicability of our formulation proposed above, we subject it to a detailed numerical analysis. In doing so, we solve Eqs. (115) and (116), numerically, to obtain the quantum and the classical rates, respectively. We study the dependence of both these rates on different parameters that are characteristic of the open quantum system.

The first of such result is obtained by analyzing the variation of the quantum and classical rates with c_0 (where $c_0^2=\gamma$ is the dissipation constant). In Fig. 1, we demonstrate the variation of the rates at three different values of T. Figures 2 and 3 show the dependence of the rates on various values of k_0 and D. In all the three cases we observe the classical rate to be always lower than the corresponding quantum rate, as the case should be. Additionally a decrease in both quantum and classical rates is envisaged as the dissipation is increased, and as a common feature we observe that these rates

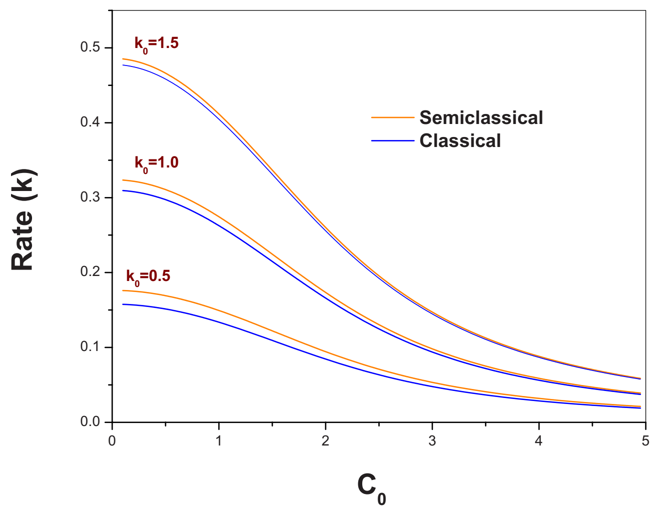

FIG. 2. (Color online) Variation of rate (k) with c_0 for different k_0 with $D=1.0$, $k_B=1.0$, $\hbar=1.0$, $T=1.0$, $\Omega_0=1.0$, $E_0=2.25$, and $\Omega_b=3.0$.

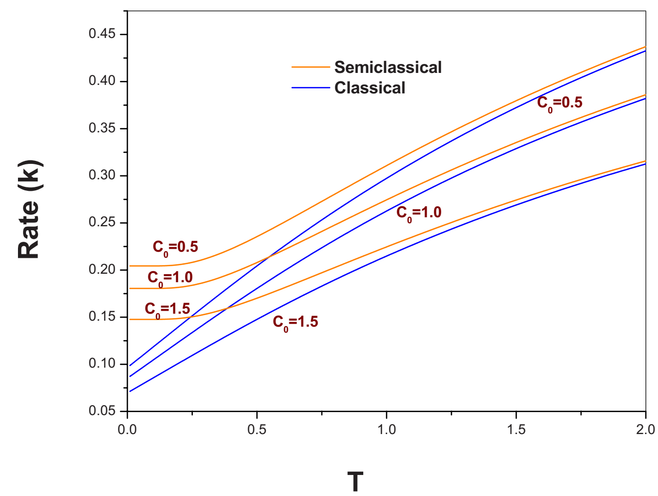

FIG. 4. (Color online) Variation of rate (k) with T for different c_0 with $D=1.0$, $k_B=1.0$, $\hbar=1.0$, $T=1.0$, $k_0=1.0$, $\Omega_0=1.0$, $E_0=2.25$, and $\Omega_b=3.0$.

fall off in a nonexponential manner since we plot the variation of the rates with c_0 instead of c_0^2. Figure 1 clearly shows that an increase of temperature increases both the rates—a commonly observed phenomenon. A close inspection of Figs. 2 and 3 reveals that both the quantum as well as the classical rates increase with increase of k_0 and D values. This is due to the fact that both k_0 and D, as in Eqs. (115) and (116), are statements of effective temperatures for the system. Thus, the effect of variation of these quantities on the rate is expected to be akin to the effect of T variation on the rates.

Figures 4–6 are the variations of rates (both classical and quantum) for different values of c_0, D, and k_0, respectively. As a common observation, in all the three cases, we envisage a monotonic increase in both the rates with the temperature, T, of the system, as is expected to be. While at lower T values, the extent of increase in the classical rate is steeper compared to the same for the quantum rate at the corresponding temperature. At high T values we experience a clear demonstration of the quantum-classical correspondence. In Figs. 5 and 6 we observe that for an increase in D and k_0 values, both the rates increase. This corroborates well with the theoretical standpoint that both D and k_0 are measures of effective temperature for the system and that the effect of variation of these will lead to the same consequence as the variation of T, as have been envisaged earlier as well.

Figures 7 and 8 represent the variation of the rates with D. Here, we observe that there is a net increase in both the quantum and classical rates as expected. The rates of increase for both classical and quantum rates occur almost similarly.

The results obtained so far are quite encouraging and clearly put forth the fact that the predictions made by our formulation are correct as far as their numerical implementation is concerned.

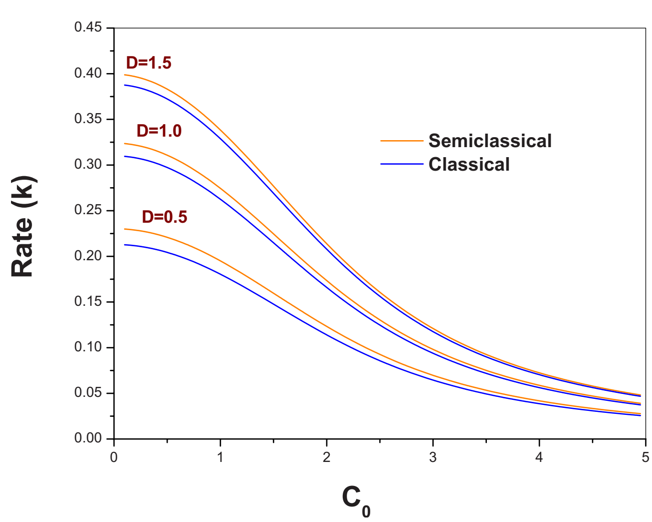

FIG. 3. (Color online) Variation of rate (k) with c_0 for different D with $k_B=1.0$, $\hbar=1.0$, $T=1.0$, $k_0=1.0$, $\Omega_0=1.0$, $E_0=2.25$, and $\Omega_b=3.0$.

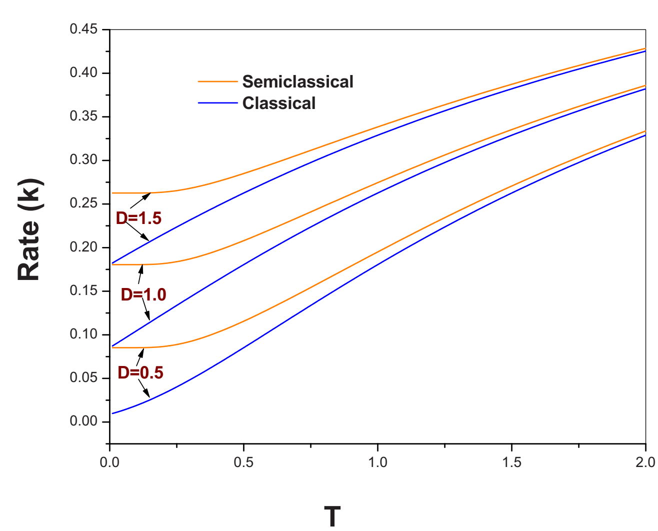

FIG. 5. (Color online) Variation of rate (k) with T for different D with $c_0=1.0$, $k_B=1.0$, $\hbar=1.0$, $T=1.0$, $k_0=1.0$, $\Omega_0=1.0$, $E_0=2.25$, and $\Omega_b=3.0$.

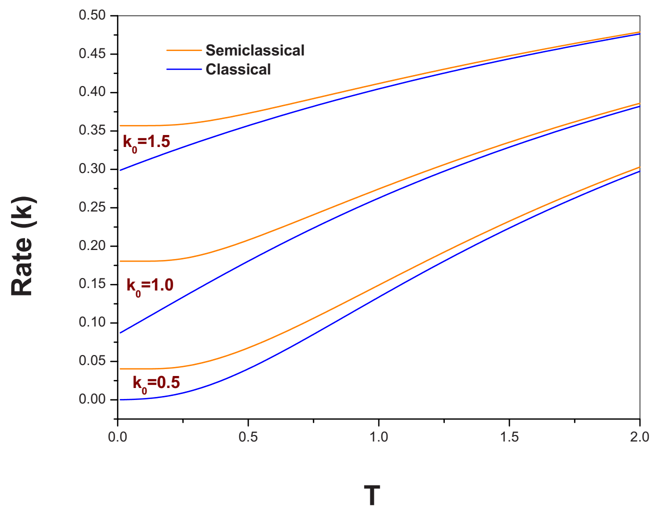

FIG. 6. (Color online) Variation of rate (k) with T for different k_0 with $c_0=1.0$, $k_B=1.0$, $\hbar=1.0$, $T=1.0$, $D=1.0$, $\Omega_0=1.0$, $E_0=2.25$, and $\Omega_b=3.0$.

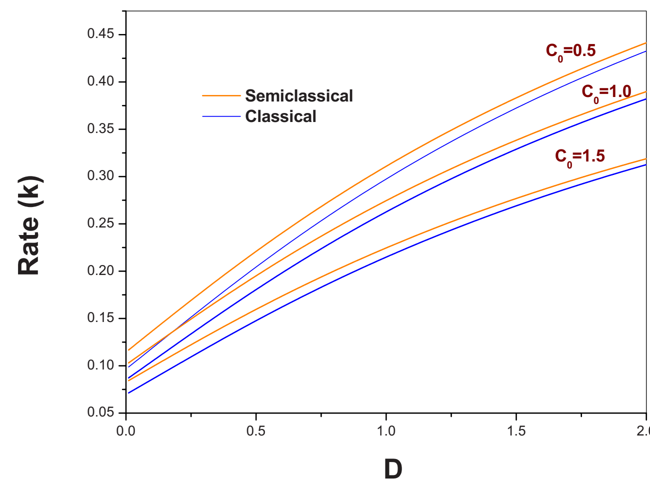

FIG. 8. (Color online) Variation of rate (k) with D for different c_0 with $T=1.0$, $k_B=1.0$, $\hbar=1.0$, $k_0=1.0$, $\Omega_0=1.0$, $E_0=2.25$, and $\Omega_b=3.0$.

VII. CONCLUSIONS

The study of thermodynamically open systems has been a subject of immense research interest during the past few decades. In this paper, we explore the possibilities associated with a system that has been made thermodynamically open by externally driving the bath rather than the system itself. There are many physical situations that are worth exploring for a better insight regarding such systems. The case of a unimolecular isomerization of a molecular species, $A \rightarrow B$, is an interesting case that may come under the purview of such a study. If this process is carried out in a photochemically active solvent, which in this case acts as the heat bath, the solvent is subject to a monochromatic light of fluctuating intensity and of a frequency that perturbs only the molecules comprising the solvent, while the actual reactant molecules remain unperturbed by this external field. As a consequence of this external disturbance, the solvent heats up due to the conversion of light energy into heat energy by the radiationless relaxation process resulting in the generation of an effective temperature like quantity owing to the constant input of energy. Since the fluctuations in the light intensity polarize the solvent molecules, the effective reaction field around the reactants gets modified. It is noteworthy that a plethora of such isomerizations or interconversions take place by surmounting an internal rotational energy barrier of approximately 0.05 eV [59]. The traditional theories of rate processes often attribute this energy requirement to be satisfied by collisions with solvent molecules. However, it is not always mandatory that the reaction rates associated with such isomerizations be enhanced via a collisional route only. In this work, on the contrary, we put forth an alternative idea of a suitable photochemically active solvent that may bring about the energy transfer in an effective manner as illustrated above and effectively enhance the reaction rate. We refer the readers to Ref. [59] for a detailed discussion along these lines.

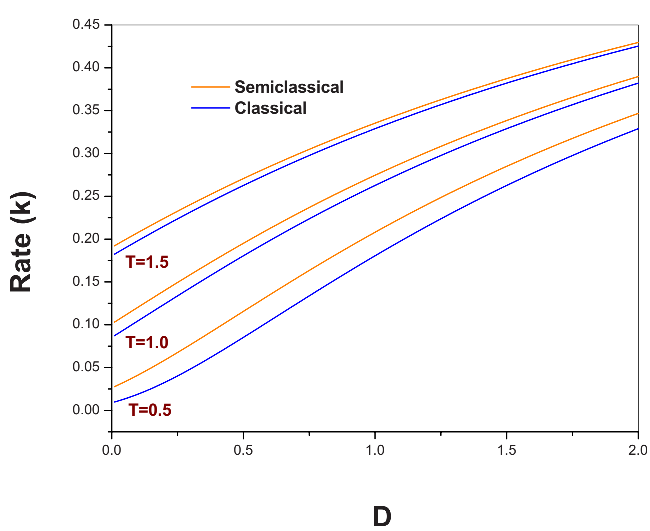

FIG. 7. (Color online) Variation of rate (k) with D for different T with $c_0=1.0$, $k_B=1.0$, $\hbar=1.0$, $k_0=1.0$, $\Omega_0=1.0$, $E_0=2.25$, and $\Omega_b=3.0$.

In this paper, we have attempted to bring to the fore the quantum effects associated with the decay rate from a metastable state of a particle which is in contact with a correlated noise-driven bath. We have achieved this by starting with a system-reservoir model to arrive at the operator-valued Langevin equation for an open quantum system where the associated heat bath is modulated by an external Gaussian noise with arbitrary decaying memory kernel. In this way, we have reached the c-number analog of this operator equation following the method of Ray *et al.* [28,29] and calculated the quantum correction terms. This was succeeded by a derivation of the quantum Fokker-Planck equation. Finally, we have applied our formulation to numerical tests and have analyzed our results.

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