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Investigation of Noise-Induced Escape Rate: A Quantum Mechanical Approach

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Abstract A quantum system coupled to a heat-bath in non-equilibrium environment is considered to study the problem of noise-induced escape rate from a metastable state in the moderate to strong friction limit (Kramers' regime). It is known that starting from an initial coherent state representation of bath oscillators, one can derive a c-number generalized quantum Langevin equation where the quantum correction terms appear as a coupled infinite set of hierarchy of equations. For practical purpose, one should truncate these equations after a certain order. In our present development, we calculate the quantum correction terms in a closed analytical form based on a systematic perturbation technique and then derive the lowest order quantum correction factor exactly in the case of an Ohmic dissipative bath. Finally, to demonstrate its applicability, the effective equation of motions has been used to study the barrier crossing dynamics which incorporates the quantum correction factors.

Keywords Quantum Langevin equation · Quantum fluctuation · Quantum corrections · Quantum escape rate · Kramers' regime

1 Introduction

The problem of quantum Langevin equation for a thermodynamically closed system has been a subject of intensive study for several research groups [1–6] during the last few decades due to its frequent appearance in the course of modelling of various phenomena, particularly in the field of lasers and optics [1–4], signal processing [5, 6], noise induce transport [7–10], spectroscopy [11–13] and so on. In the recent years, the subject has gained considerable interest due to a vast experimental progress which allows for the tailoring and

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manipulation of quantum matter. In mesoscopic physics, for instance, super-conducting circuits have been realized to observe coherent dynamics and entanglement [14]. 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 [15]. Typically, these systems are in contact with a large number of environmental degrees of freedom, e.g. electromagnetic modes of the circuitry or residual vibronic modes which gives to decoherence and relaxation [16].

For microscopic description of additive noise and linear dissipation which 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 eighties by Calderia and Legget [17] which found wide applications 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 seventies to treat quantum nonlinear phenomena with considerable success. The method which received major appreciation afterwards in the wide community of physicists and chemists is the real time functional integrals [18]. Notwithstanding the phenomenal 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 probability distribution function of a particle executing Brownian motion in a forced field, the path integral method relies on the evolution of quantum partition function of the systems interacting with heat-bath consisting of harmonic oscillators with natural extension of the classical method to quantum domain.

In the standard approach to open quantum systems, the reduced dynamics of the system of interest is obtained by tracing out the reservoir degrees of freedom from the conservative system-plus-reservoir dynamics. Alternatively, the programme can be carried out through path integral expressions for the reduced density matrix [19]. The distinguishing feature of the dissipative path integrals is an influence functional which describes self-interactions nonlocal in time. Hence, a simple quantum mechanical analogue to the classical Langevin equation is not known. Commonly used equations, such as master or Redfield equation [20] in the weak coupling case and quantum Smoluchowski equations [21] rely on perturbation theory. In intermediates domains, quantum Monte Carlo techniques have been put forward for tight binding systems, but achievable propagation times are severely limited by the dynamical sign problem [22, 23]. Recently, it has been shown that the influence functional can be exactly reproduced through stochastic averaging of a process without explicit memory [24, 25]. The formulation turned out to be particularly efficient for weak to moderate friction and low temperature [25, 26], a regime which lies beyond the validity of Redfield equations, on the one hand, and beyond the applicability of Monte Carlo schemes, on the other [22, 23]. For non-linear systems, the main objection of the Monte Carlo simulation is that the convergence of the stochastic average for relatively long times is still an unsolved problem, barring some progress for the spin-boson system, by using hierarchic approaches to quantum memory terms [27]. A reliable and efficient generally applicable method to tackle the dissipative dynamics is still missing. In this article we address the issue of handling quantum dissipative dynamics, even for nonlinear system, when classical statistical mechanical tools can be used, particularly in the context of noise-induced transport.

The rest of the paper is organized as follows. Based on a system-reservoir coupling model, we develop and describe the quantum Langevin equation for a Brownian particle and then we obtain the c-number analogue of this operator equation in Sect. 2. In Sect. 3, we

derive the Fokker-Planck equation for a quantum Brownian particle moving in an external force. Section 4 comprises the calculation of the quantum correction terms (which appear as a closed analytical form) via a perturbative approach. Using these quantum corrections, we solve the corresponding Kramers' equation to study the barrier crossing dynamics in Sect. 5. The paper has been concluded in Sect. 6.

2 The Transition from Operator Quantum Langevin Equation to Its *c*-Number Form

We start this section through a brief discussion of constructing the c-number formulation of quantum dissipative dynamics, originally put forward by Ray and co-workers [28] in the context of quantum state dependent diffusion. A particle of unit mass is connected to a hat bath comprising of a set of harmonic oscillators of unit mass with frequency set $\{\omega_j\}$. The total system-bath Hamiltonian can be written in the Zwanjig form [29] as

$$\hat{H} = \frac{\hat{p}^2}{2} + V(\hat{x}) + \sum_j \left[\frac{\hat{p}_j^2}{2} + \frac{1}{2}\left(\hat{q}_j - \frac{c_j}{\omega_j^2}\hat{x} \right)^2 \right] \tag{1}$$

where $\hat{x}$ and $\hat{p}$ are coordinate and momentum operators of the Brownian particle, $\{\hat{q}_j, \hat{p}_j\}$ is the set of coordinate and momentum operators for the heat-bath oscillators, $V(\hat{x})$ is the potential that exerts external force field on the system. This system is coupled to the heat-bath linearly via the coupling constant c_j. The coordinate and momentum operators follow the usual commutation relations:

$$[\hat{x}, \hat{p}] = i\hbar, \qquad [\hat{q}_j, \hat{p}_k] = i\hbar\delta_{jk} \tag{2}$$

Eliminating the reservoir degrees of freedom in the usual way [18, 30], we obtain the operator quantum Langevin equation corresponding to Hamiltonian (1) as follows:

$$\ddot{\hat{x}} + \int_0^t dt' \gamma(t-t')\dot{\hat{x}}(t') + V'(x') = \hat{\xi}(t) \tag{3}$$

where, the noise operator $\hat{\xi}(t)$ and the memory kernel $\gamma(t)$ are given by

$$\hat{\xi}(t) = \sum_j c_j \left[\left(\hat{q}_j(0) - \frac{c_j}{\omega_j^2}\hat{x}(0) \right) \cos(\omega_j t) + \frac{\hat{p}_j(0)}{\omega_j} \sin(\omega_j t) \right] \tag{4}$$

$$\gamma(t) = \sum_j \frac{c_j^2}{\omega_j^2} \cos(\omega_j t) \tag{5}$$

Equation (3) is an exact generalized quantum Langevin equation in operator form [31]. Following the method of Ray and co-workers [28], we now replace (3) by its c-number equivalent. We introduce product separable quantum states of the particle and the bath oscillators at $t = 0$,

$$|\psi\rangle = |\phi\rangle\{|\alpha_j\rangle\} \tag{6}$$

where $|\phi\rangle$ denotes any arbitrary initial state of the particle and $\{|\alpha_j\rangle\}$ corresponds to the initial coherent state of the jth oscillator. Here, $\{|\alpha_j\rangle\}$ is given by

$$\{|\alpha_j\rangle\} = \exp\left(-\frac{1}{2}|\alpha_j|^2\right) \sum_{n_j=0}^{\infty} \left(\frac{\alpha_j^{n_j}}{\sqrt{n_j!}}\right) |n_j\rangle \tag{7}$$

and α_j is expressed in terms of the mean values of the coordinate and momentum of the jth oscillator:

$$\langle q_j(0)\rangle - \langle \hat{x}(0)\rangle = \sqrt{\frac{\hbar}{2\omega_j}}(\alpha_j + \alpha_j^{\star}) \tag{8}$$

$$\langle \hat{p}_j(0)\rangle = -i\sqrt{\frac{\hbar\omega_j}{2}}(\alpha_j - \alpha_j^{\star}) \tag{9}$$

Now, following the work of Ray and co-workers [28] and doing the quantum-statistical averaging starting from an initial product separable quantum state [28], one obtains the c-number generalized quantum Langevin equation:

$$\ddot{q}(t) + \int_0^t dt' \gamma(t-t')\dot{q}(t') + V(q') = \xi(t) + Q_V(q,t) \tag{10}$$

where

$$q(t) = \langle \hat{x}(t)\rangle \tag{11}$$

$$\xi(t) = \langle \hat{\xi}(t)\rangle = \sum_j \left[\left\{\langle \hat{q}_j(0)\rangle - \langle \hat{x}(0)\rangle\right\} \frac{c_j}{\omega_j^2} \cos(\omega_j t) + \sqrt{\frac{c_j}{\omega_j^2}} \langle \hat{p}_j(0)\rangle \sin(\omega_j t) \right] \tag{12}$$

Q_V denote the quantum correction terms, given by

$$Q_V(q,t) = V'(q,t) - \langle V'(\hat{x},t)\rangle \tag{13}$$

In order that $\xi(t)$ be an effective c-number noise we must have

$$\langle \xi(t)\rangle_S = 0 \tag{14}$$

$$\langle \xi(t)\xi(t')\rangle_S = \frac{1}{2}\sum_j \frac{c_j}{\omega_j^2}\hbar\omega_j \coth\left(\frac{\hbar\omega}{2k_BT}\right)\cos\omega_j(t-t') \tag{15}$$

$\langle\cdots\rangle$ denotes statistical average over the initial distribution of the mean values of the moments and coordinates of the bath oscillators. Equations (14) and (15) imply that $\xi(t)$ is centered around zero and satisfies the quantum fluctuation dissipation relation, and is obtained if and only if the initial quantum mechanical mean values of momenta and coordinates of the bath oscillators have the following distribution [28]

$$\mathcal{P}_j = N \exp\left[-\frac{\omega_j^2\{\langle \hat{q}_j(0)\rangle - \langle \hat{x}_j(0)\rangle\}^2 + \langle \hat{p}_j(0)\rangle^2}{2\hbar\omega_j(\bar{n}_j + \frac{1}{2})} \right] \tag{16}$$

where N is the normalization constant and

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

is the average photon number at temperature T. The statistical average of any quantum mechanical mean value of any observable O_j is defined as

$$\langle O_j(0)\rangle_S = \int O_j \mathcal{P}_j d\langle\hat{p}_j(0)\rangle d\{\langle\hat{q}_j(0)\rangle - \langle\hat{x}(0)\rangle\} \tag{17}$$

Using (11), (16) and (17) one can then easily show the properties (14) and (15) of the c-number noise. At this juncture, it is important to note that $\mathcal{P}_j$ is a canonical Wigner distribution for a displaced harmonic oscillator which always remains positive [32]. Now, one can identify (10) as a c-number generalized quantum Langevin equation which is governed by the c-number quantum noise $\xi(t)$ originating from the heat-bath and is characterized by the properties (14) and (15). The quantum fluctuation term $Q_V(q,t)$ originates from the nonlinearity of the potential.

3 Quantum Fokker-Planck Equation

The classical Kramers's equation forms the dynamical basis of our understanding of noise-induced escape from a metastable state. It is interesting to note that although classical Kramers' equation was proposed more than sixty years ago, hopeful developments have been recently reported in the direction of quantum mechanical analogue of the Kramers' model. The quantum Kramers' theory of reaction rate was developed primarily within path integral framework. The validity of the major results is restricted to activated tunnelling regime, i.e., above the cross-over temperature. The formation of 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 tunnelling as well as for the non-Markovian regime. We consider (10) 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

$$V(q) = V(0) + \frac{1}{2}\omega^2 q^2 + V_N(q) \tag{18}$$

where $V_N(q)$ is the total nonlinear contribution and ω_0^2 refers to $V''(0)$. With the help of (18), the Langevin equation may be rewritten as

$$\ddot{q} + \omega_0^2 q + \int_0^t dt'\gamma(t-t')\dot{q}(t') = -V_N'(q) + Q_V(q,t) + \xi(t) \tag{19}$$

The two potential dependent terms on the right-hand side of (19) can be evaluated as a function of t so that we may treat the entire right-hand side including $\xi(t)$ as an inhomogeneous contribution. We therefore write

$$\ddot{q} + \omega_0^2 q + \int_0^t dt'\gamma(t-t')\dot{q}(t') = Q_T(t) + \xi(t) \tag{20}$$

where $Q_T(t) = Q_V(t) - V_N'(q)$. Laplace transform of (20) leads to the following

$$q(t) = \langle q(t)\rangle_S + \int_0^t c_p(t-\tau)\xi(\tau)d\tau \tag{21}$$

where

$$\langle q(t)\rangle_S = q(0)c_q(t) + p(0)c_p(t) + G(t) \tag{22}$$

$$G(t) = \int_0^t c_p(t-\tau)\,Q_T(\tau)d\tau \tag{23}$$

$$c_q(t) = 1 - \omega_0^2 \textstyle\int_0^t d\tau c_p(\tau) \tag{24}$$

where

$$c_p(t) = L^{-1}\left[\frac{1}{s^2 + s\widetilde{\gamma}(s) + \omega_0^2}\right] \tag{25}$$

Here, L^{-1} denotes the inverse of Laplace transformation and $\widetilde{\gamma}(s)$ is the Laplace transform of the memory kernel $\gamma(t)$:

$$\widetilde{\gamma}(s) = \int_0^\infty \exp(-st)\gamma(t)dt \tag{26}$$

Time derivative of (21) gives

$$p(t) = \langle p(t)\rangle_S + \int_0^t \dot{c}_p(t-\tau)\xi(\tau)d\tau \tag{27}$$

where

$$\langle p(t)\rangle_s = p(0)\dot{c}_p(t) - q(0)\omega_0^2 c_p(t) + g(t) \tag{28}$$

with

$$g(t) = \dot{G}(t) \tag{29}$$

In the above expressions, c_p and $\hat{c}_p(t)$ are the relaxation functions and $G(t)$ is a convolution integral which describes the interplay between nonlinearity, quantum effects and relaxation. Now using the symmetry properties of the correlation function $\langle\xi(t)\xi(t')\rangle_S$ and the solution for $q(t)$ and $p(t)$, we have the following expressions for the variances

$$\begin{aligned}\sigma_{qq}^2(t) &= \left\langle\left[q(t) - \langle q(t)\rangle_S\right]^2\right\rangle_S \\ &= 2\int_0^t dt_1 c_p(t_1)\int_0^{t_1} c_p(t_2)c(t_1-t_2)dt_2\end{aligned} \tag{30}$$

$$\begin{aligned}\sigma_{pp}^2(t) &= \left\langle\left[p(t) - \langle p(t)\rangle_S\right]^2\right\rangle_S \\ &= 2\int_0^t dt_1 \dot{c}_p(t_1)\int_0^{t_1} \dot{c}_p(t_2)c(t_1-t_2)dt_2\end{aligned} \tag{31}$$

and

$$\sigma_{pq}^2(t) = \left\langle \left[q(t) - \langle q(t)\rangle_S\right]^2 \left[p(t) - \langle p(t)\rangle_S\right]^2 \right\rangle_S$$
$$= 2\int_0^t dt_1 c_p(t_1) \int_0^{t_1} \dot{c}_p(t_2) c(t_1 - t_2) dt_2 \tag{32}$$

where

$$\langle \xi(t)\xi(t')\rangle = c(t - t') \tag{33}$$

Having obtained the expression for the statistical average and variance, we are now in a position to write down the quantum Kramers' equation which is a Fokker-Planck description of the probability density function $\rho(q, p, t)$ of the quantum mechanical mean values of the coordinate and momentum operators of the particle. Assuming the statistical description of noise $\xi(t)$ to be Gaussian, we define the joint characteristic function $\widetilde{P}(\mu, \rho, t)$ where (q, μ) and (p, ρ) are Fourier transform pair of variables. Then, using the standard procedure [33], we arrive at the equation of motion for probability distribution function $P(q, p, t)$ which is the inverse Fourier transform of $\widetilde{P}(\mu, \rho, t)$,

$$\frac{\partial P(q, p, t)}{\partial t} = \frac{\partial}{\partial q}\left[\{-p + g(t)\}P(q, p, t)\right]$$
$$+ \frac{\partial}{\partial p}\left[\{\widetilde{V}'(q) + \Omega(t) - N(t)\}P(q, p, t)\right]$$
$$+ \frac{\partial}{\partial p}\left[\epsilon(t)p\right]P(q, p, t) + \phi(t)\frac{\partial^2}{\partial p^2}P(q, p, t) + \psi(t)\frac{\partial^2}{\partial p \partial q}P(q, p, t) \tag{34}$$

where

$$\epsilon(t) = -\frac{d}{dt}\left[\ln Y(t)\right] \tag{35a}$$

$$Y(t) = \frac{\dot{c}_p(t)}{\omega_0^2}c_q(t) + c_p^2(t) \tag{35b}$$

$$\widetilde{\omega}_0^2(t) = \frac{1}{Y(t)}\left[-c_p(t)\ddot{c}_p(t) + \dot{c}_p^2(t)\right] \tag{35c}$$

$$N(t) = \frac{1}{Y(t)}\left[-\frac{1}{\omega_0^2}g(t)\ddot{c}_p(t)c_q(t) + \dot{c}_p^2(t)G(t)\right] \tag{35d}$$

$$\Omega(t) = c_p(t)\frac{d}{dt}\left[G(t)\dot{c}_p(t)\right] \tag{35e}$$

$$\phi(t) = \widetilde{\omega}_0^2(t)\sigma_{qp}^2(t) + \epsilon(t)\sigma_{pp}^2(t) + \frac{1}{2}\dot{\sigma}_{pp}^2(t) \tag{35f}$$

$$\psi(t) = \dot{\sigma}_{qp}^2(t) + \epsilon(t)\sigma_{qp}^2(t) + \widetilde{\omega}_0^2(t)\sigma_{qq}^2(t) - \sigma_{pp}^2(t) \tag{35g}$$

$\widetilde{V}'(q)$ is the renormalized potential linearized at $q = 0$, the frequency being $\widetilde{\omega}_0^2$ as given by (35c). The Fokker-Planck equation (34) is the quantum mechanical version of classical non-Markovian Kramers' equation and is valid for arbitrary temperature and friction. It is

interesting to note that due to its explicit dependence of Q_T, the quantities $g(t)$, $\Omega(t)$, and $N(t)$ manifestly include quantum effects through the nonlinearity of the system potential. In the classical limit, the anharmonicity vanishes and for $k_BT \gg \hbar\omega_0$, $\phi(t)$ and $\psi(t)$ reduce to the forms that can be obtained by applying classical fluctuation-dissipation relation in (35f) and (35g). Consequently, the quantum Kramers' equation reduces exactly to non-Markovian classical Kramers' equation derived earlier by Aledman and Mazo [34–36] for harmonic potential.

To proceed further it is worth noting that the classical-like stochastic differential equation, (20) contains essential quantum features, though the term $\xi(t)$ 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 nonlinearity and the quantum effects are entangled in the latter quantity modifying the classical part of the potential. Thus the classical potential force $-V'(x,t)$ is modified by the quantum dispersion term. In absence of quantum dispersion term, Q_V and with $D_0 \to \gamma k_BT$ as one approaches the classical limit [$k_BT \gg \hbar\Omega_0$; where Ω_0 is the average bath frequency] the quantum Langevin equation reduces to classical one [37].

4 Quantum Correction Terms

Referring to the quantum nature of the system in the Heisenberg picture, we now write the system operators $\hat{x}$ and $\hat{p}$ as

$$\hat{x}(t) = q(t) + \delta\hat{x}(t), \qquad \hat{p}(t) = p(t) + \delta\hat{p}(t) \tag{36}$$

where $q(=\langle\hat{x}\rangle)$ and $p(=\langle\hat{p}\rangle)$ are the quantum mechanical mean values, and $\delta\hat{x}$ and $\delta\hat{p}$ are the operators and they are quantum fluctuations around their respective mean values. By construction they also follow:

$$\langle\delta\hat{x}\rangle = 0 = \langle\delta\hat{p}\rangle, \qquad \left[\delta\hat{x}, \delta\hat{p}\right] = i\hbar$$

Now using (36) and a Taylor series expansion around q, one obtains

$$Q_V(q,t) = -\sum_{n\geq 2} \frac{1}{n!} V^{(n+1)}(q)\langle\delta\hat{x}^n(t)\rangle \tag{37}$$

where $V^{(n+1)}(q)$ is the $(n+1)$-th derivative of the potential $V(q)$. The calculation of $Q_V(q,t)$ depends on quantum correction factor $\langle\delta\hat{x}^n(t)\rangle$ which may be obtained by solving the quantum corrections.

Putting (36) in (3) one can easily show that the quantum correction equation is given by

$$\delta\ddot{\hat{x}}(t) + \int_0^t dt'\gamma(t-t')\delta\dot{\hat{x}}(t') + V''(q)\delta\hat{x}(t) + \sum_{n\geq 2}\frac{1}{n!}V^{(n+1)}(q)\langle\delta\hat{x}^n(t)\rangle = \delta\hat{\epsilon}(t) \tag{38}$$

where $\delta\hat{\epsilon}(t) = \hat{\epsilon}(t) - \epsilon(t)$. For solving the Kramers' equation to get the barrier crossing dynamics, it is customary to linearize the potential around the potential well and also around the top of the potential barrier [33, 36]. Thus to calculate the quantum correction terms, it is sufficient to consider that the confining potential is harmonic: $V(q) = V(0) + \frac{1}{2}\omega_0^2 q^2$ and consequently, (38) becomes

$$\delta\ddot{\hat{x}}(t) + \int_0^t dt'\gamma(t-t')\delta\dot{\hat{x}}(t') + \omega_0^2\delta\hat{x}(t) = \delta\hat{\epsilon}(t) \tag{39}$$

Since we calculate $\delta\ddot{\hat{x}}(t)$ in a perturbative way, we restrict our calculation to the leading order of the quantum correction factors, i.e.,

$$Q_V(q,t) = -\frac{1}{2}V'''(q)\langle\delta\hat{x}^2(t)\rangle \tag{40}$$

Thus, it is now adequate to derive only $\langle\delta\hat{x}^2(t)\rangle$ for the calculation of quantum correction factors.

With the above mentioned approximations, the quantum correction equation becomes

$$\delta\ddot{\hat{x}}(t) + \int_0^t dt'\gamma(t-t')\delta\dot{\hat{x}}(t') + \omega_0^2\delta\hat{x}(t) = \delta\hat{\epsilon}(t) \tag{41}$$

The solution of (41) is

$$\delta\hat{x}(t) = h_1(t)\delta\hat{x}(0) + h_2(t)\delta\dot{\hat{x}}(0) + \int_0^t dt' h_2(t-t')\delta\hat{\xi}(t') \tag{42}$$

where $h_1(t)$ and $h_2(t)$ are the inverse Laplace transformation of $\widetilde{h}_1(s)$ and $\widetilde{h}_2(s)$ respectively where

$$\widetilde{h}_1(s) = \frac{s+\widetilde{\gamma}(s)}{s+s\widetilde{\gamma}(s)+\omega_0^2} \tag{43}$$

$$\widetilde{h}_2(s) = \frac{1}{s+s\widetilde{\gamma}(s)+\omega_0^2} \tag{44}$$

with

$$\widetilde{\gamma}(s) = \int_0^\infty \gamma(t)\exp(-st)dt \tag{45}$$

being the Laplace transformation of the frictional kernel $\gamma(t)$. Squaring (42) and taking the quantum statistical average, we obtain the relevant quantum correction $\langle\delta\hat{x}^2(t)\rangle$ as follows:

$$\begin{aligned}\langle\delta\hat{x}^2(t)\rangle = {} & h_1^2(t)\langle\delta\hat{x}^2(0)\rangle + h_2^2(t)\langle\delta\hat{p}^2(0)\rangle \\ & + h_1(t)h_2(t)\langle\big(\delta\hat{x}(0)\delta\hat{p}(0) + \delta\hat{p}(0)\delta\hat{x}(0)\big)\rangle \\ & + 2\int_0^t dt'\int_0^{t'} dt'' h_2(t-t')h_2(t-t'')\langle\delta\hat{\xi}(t')\delta\hat{\xi}(t'')\rangle\end{aligned} \tag{46}$$

A standard choice of initial conditions corresponding to minimum uncertainty state is [28, 38].

$$\langle\delta\hat{x}^2(0)\rangle = \frac{\hbar}{2\omega_0}, \qquad \langle\delta\hat{p}^2(0)\rangle = \frac{\hbar\omega_0}{2}, \qquad \big\langle\big(\delta\hat{x}(0)\delta\hat{p}(0) + \delta\hat{x}(p)\delta\hat{x}(0)\big)\big\rangle = \hbar \tag{47}$$

We would like to know the exact form of the function $h_1(t)$ and $h_2(t)$ in order to calculate $\langle\delta\hat{x}^2(t)\rangle$. From the definition of $h_1(t)$ and $h_2(t)$, we have

$$h_1(t) = \frac{1}{2\pi i}\int_{-i\infty+\epsilon}^{i\infty+\epsilon}\widetilde{h}_1(s)\exp(st)ds \tag{48a}$$

$$h_2(t) = \frac{1}{2\pi i}\int_{-i\infty+\epsilon}^{i\infty+\epsilon}\widetilde{h}_2(s)\exp(st)ds \tag{48b}$$

Using the residue one can easily show that for the Ohmic dissipative bath underdamped case:

$$h_1(t) = \exp\left(-\frac{\gamma t}{2}\right)\left[\cos(\omega_1 t) + \frac{\gamma}{2\omega_1}\sin(\omega_1 t)\right] \tag{49a}$$

$$h_2(t) = \exp\left(-\frac{\gamma t}{2}\right)\left[\frac{1}{\omega_1}\sin(\omega_1 t)\right] \tag{49b}$$

where $\omega_1 = \pm\sqrt{(\omega_0^2 - \gamma^2/4)}$. Now for the Ohmic heat-bath, the double integral in (46) can be written as

$$\begin{aligned}
&2\int_0^t dt' \int_0^{t'} dt'' h_2(t-t')h_2(t-t'')\langle\delta\hat{\xi}(t')\delta\hat{\xi}(t'')\rangle \\
&= \frac{\gamma}{\pi}\int_0^\infty d\omega\hbar\omega\coth\left(\frac{\hbar\omega}{2k_BT}\right)\int_0^t dt' \int_0^{t'} dt'' \exp\left(-\frac{\gamma(t-t')}{2}\right) \\
&\quad\times\left[\frac{\sin\omega(t-t')}{\omega_1}\exp\left(-\frac{\gamma(t-t'')}{2}\right)\frac{\sin\omega(t-t'')}{\omega_1}\cos\omega(t'-t'')\right] \\
&= \frac{\gamma}{\pi}\int_0^\infty d\omega\hbar\omega\coth\left(\frac{\hbar\omega}{2k_BT}\right)\left|\frac{1 - e^{[-(\gamma/2-i\omega)t]}[\cos\omega_1 t + (\gamma/2 - i\omega_1)\frac{\sin\omega_1 t}{\omega_1}]}{\omega^2 - \omega_0^2 + i\gamma\omega}\right|^2
\end{aligned} \tag{50}$$

From (50), we observed that the time dependence of the mean fluctuation in displacement is complicated, but it reduces to a simple form for large time compared to γ^{-1} and is given by

$$\langle\delta\hat{x}^2\rangle_{\rm eq} = \frac{\gamma}{\pi}\int_0^\infty d\omega\left\{\hbar\omega\coth\left(\frac{\hbar\omega}{2k_BT}\right)\frac{1}{(\omega^2-\omega_0^2)^2 + (\gamma\omega)^2}\right\} \tag{51}$$

In the classical limit (i.e., for $\hbar \to 0$) we find

$$\langle\delta\hat{x}^2\rangle_{\rm eq} = \frac{k_BT}{\omega_0^2}$$

which is the classical equipartition result. In the weak damping regime ($\gamma < \omega$), one obtains from (51)

$$\langle\delta\hat{x}^2\rangle_{\rm eq} = \frac{\hbar}{2\omega_0}\coth\left(\frac{\hbar\omega_0}{2\pi k_BT}\right) \tag{52}$$

5 Barrier Crossing Dynamics

We now turn to the problem of decay of a meta-stable state. We consider a particle of unit mass moving in a cubic potential of the form

$$V(q) = \frac{-1}{3}Aq^3 + Bq^2 \tag{53}$$

where q now corresponds to the reaction coordinate, and its values at the extrema of the potential at $q = 0$ and $q = q_b$ denote the reactant and the transition state, respectively. In this model, all the remaining degrees of freedom of the system and the environment constitute a heat-bath at a finite temperature T.

Before proceeding further, we return to (5) and (15). To obtain a finite result in the continuum limit, the coupling function $c_j = c(\omega)$ is chosen as

$$c(\omega) = \frac{c_0 \omega}{\sqrt{\tau_c}}$$

With this choice $\gamma(t)$ reduces to the following form:

$$\gamma(t) = \frac{c_0^2}{\tau_c} \int_0^\infty d\omega \mathcal{D}(\omega) \cos(\omega t) \tag{54}$$

where c_0 is some constant and $\omega_c = \frac{1}{\tau_c}$ is the cutoff frequency of the bath oscillators. τ_c may be regarded as the correlation time of the bath and $\mathcal{D}$ is the density of modes of the heat-bath which is assumed to be Lorentzian:

$$\mathcal{D}(\omega) = \frac{2}{\pi} \frac{1}{\tau_c(\omega^2 + \tau_c^{-2})}$$

With these forms of $\mathcal{D}$ and $c(\omega)$, $\gamma(t)$ takes the form:

$$\gamma(t) = \frac{c_0^2}{\tau_c} \exp(-t/\tau_c) = \frac{\gamma}{\tau_c} \exp(-t/\tau_c) \tag{55}$$

where $c_0^2 = \gamma$. For $\tau_c \to 0$, (55) reduces to

$$\gamma(t) = 2\gamma\delta(t) \tag{56}$$

and the noise correlation function, (15) becomes

$$\langle \xi(t)\xi(t') \rangle_S = \frac{\gamma}{2\tau_c} \int_0^\infty d\omega \left\{ \hbar\omega \coth\left(\frac{\hbar\omega}{2k_B T}\right) \cos\omega(t-t') \mathcal{D}(\omega) \right\} \tag{57}$$

Equation (57) is an exact expression for two-time correlation. We now make the following assumption. As $\hbar\omega \coth(\frac{\hbar\omega}{2k_B T})$ is a much more smooth function of ω, at least for not too low temperatures, the integral in (57) can be approximated as [28]

$$\langle \xi(t)\xi(t') \rangle_S \simeq \frac{\gamma}{2\tau_c} \hbar\Omega_0 \coth\left(\frac{\hbar\Omega_0}{2k_B T}\right) \int_0^\infty d\omega \cos\omega(t-t') \mathcal{D}(\omega)$$

where Ω_0 is the average bath frequency. Thus, we have in the limit $\tau_c \to 0$,

$$\langle \xi(t)\xi(t') \rangle_S = 2D_0 \delta(t-t') \tag{58}$$

where

$$D_0 = \frac{\gamma}{2} \hbar\Omega_0 \left[\overline{n}(\Omega_0) + \frac{1}{2} \right] \tag{59}$$

Here, it is important to note that our above assumption is not valid for very low temperatures. In this sense, our following development does not account the dynamics which is fully quantum mechanical in nature. Nevertheless, the Ansatz, (16), which is the canonical thermal Wigner distribution function for a harmonic oscillator system always remains positive definite, containing the quantum information of the heat-bath comprised of a set of quantum mechanical harmonic oscillator. A special advantage of using this distribution function is that it remains valid as a pure state nonsingular distribution function even at $T = 0$. Thus, from the very mode of our development, apart from the assumption regarding two-time correlation function, (58), rest of our treatment is truly quantum mechanical.

With the above mentioned scheme and for Ohmic dissipative bath (34) (i.e. the quantum Kramers' equation) reads [28]

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial q}(pP) + \frac{\partial}{\partial p}\left[\gamma p + V'(q) - Q_V\right]P + D_0\frac{\partial^2 P}{\partial p^2} \tag{60}$$

Now linearizing the above equation near the bottom of the potential well one obtains the approximate equation for the evolution of probability distribution function near the bottom of the potential well,

$$\frac{\partial P^0}{\partial t} = -p\frac{\partial P^0}{\partial q} + \gamma P^0 + \left[\gamma p + \omega_0^2 q - Q_V\right]\frac{\partial P^0}{\partial p} + D_0\frac{\partial^2 P^0}{\partial p^2} \tag{61}$$

In the steady state, (61) becomes

$$\frac{\partial}{\partial t}P^0_{\mathrm{St}}(q,p) = -p\frac{\partial P^0}{\partial q} + \gamma P^0 + \left[\gamma p + \omega_0^2 q - Q_V^0\right]\frac{\partial P^0}{\partial p} + D_0\frac{\partial^2 P^0}{\partial p^2} \tag{62}$$

where Q_V^0 represents the equilibrium value of $Q_V(q,p)$. The steady state solution of (61) is given by

$$P^0_{\mathrm{St}}(q,p) = \frac{1}{Z}\exp\left[-\left(\frac{p^2}{2D_0} + \frac{\omega_0^2 q^2 - 2Q_V^0 q}{2D_0}\right)\right] \tag{63}$$

and can be checked directly from (62) and (63). Equation (63) is the quantum mechanical analogue of the classical equilibrium Boltzmann distribution, $\exp[-\frac{(\frac{p^2}{2}+V(q))}{k_BT}]$. In the classical limit, the thermal fluctuation is presented by the unique quantity k_BT whereas, in the present case, we have the quantity D_0 which contains the information of thermal fluctuations as well as the quantum fluctuations along with the effects of nonlinearity of the system potential through the term Q_V. As we will see later, this leads to the recovery of the classical rate expression in the high temperature limit. Now, linearizing the potential $V(q)$ near the top of the barrier (at $q = q_b$), we get the equation of probability distribution function near the barrier top [with $V(y) = V_b - \frac{1}{2}\omega_b^2 y^2$; $\omega_b^2 > 0$]:

$$\frac{\partial P^b}{\partial t} = -p\frac{\partial P^b}{\partial q} + \gamma P^b + \left[\gamma p - \omega_b^2 y - Q_V\right]\frac{\partial P^b}{\partial p} + D_0\frac{\partial^2 P^b}{\partial p^2} \tag{64}$$

Following Kramers' we assume that the stationary solution of (64) is given by

$$P^b_{\mathrm{St}}(q,p) = \exp\left[-\left(\frac{p^2}{2D_0} + \frac{\omega_b^2 y^2 - 2Q_V^0 y}{2D_0}\right)\right]F(q,p) \tag{65}$$

with $y = (q - q_b)$. The auxiliary function $F(q,p)$ satisfies the equation

$$D_0\frac{\partial^2 F}{\partial p^2} - p\frac{\partial F}{\partial y} - \left[\gamma p + \omega_b^2 y + Q_V^0\right]\frac{\partial F}{\partial p} = 0 \tag{66}$$

On letting $u = p + ay$, where a is a constant to be determined, the above (66) reduces to

$$D_0\frac{d^2 F}{du^2} - \left[(\gamma + a)p + \omega_b^2 y^2 + Q_V^0\right]\frac{dF}{du} = 0 \tag{67}$$

Let us now consider

$$\omega_b^2 y + \Gamma p = -\lambda u \tag{68}$$

where $\Gamma = (\gamma + a)$ and λ is another constant. Then (67) becomes

$$\frac{d^2F}{du^2} + (\Lambda u + \alpha)\frac{dF}{du} = 0 \tag{69}$$

with

$$\lambda = \Lambda D_0, \qquad \alpha = \frac{Q_V^0}{D_0} \tag{70}$$

The quantities λ and a are related by $-\lambda = \gamma + a$ and consequently a satisfies the equation:

$$a^2 + \gamma a - \omega_b^2 = 0$$

so that the two roots of a are

$$a_\pm = \frac{1}{2}\left[-\gamma \pm \sqrt{(\gamma^2 + 4\omega_b^2)}\right]$$

The general solution of (69) is given by

$$F(u) = F_2 \int_0^u du \exp\left[-\frac{\Lambda}{2}u^2 - \alpha u\right] + F_1 \tag{71}$$

where F_1 and F_2 are two arbitrary constants. This solution must vanish at $|u| \to +\infty$ which implies Λ should be positive definite and consequently the negative value of a i.e. a_- should be taken as the relevant root. Now, the requirement that F vanishes for large q yields the relation between the two constants F_1 and F_2 as

$$F_1 = F_2\sqrt{\frac{\pi}{2\Lambda}} \exp\left(\frac{\alpha^2}{2\pi}\right)\left[1 - \Phi\left(\frac{\alpha}{2\pi}\right)\right] \tag{72}$$

where Φ is the probability integral:

$$\Phi(x) = \frac{2}{\sqrt{\pi}} \int_0^x dt \exp(-t^2)$$

Hence, the stationary expression of probability density function near the top of the barrier is given by

$$P_{\mathrm{St}}^b(q, p) = F_2\sqrt{\frac{\pi}{2\Lambda}} \exp\left(\frac{\alpha^2}{2\pi}\right)\left[1 - \Phi\left(\frac{\alpha}{2\pi}\right)\right] + \int_0^u du \exp\left[-\frac{\Lambda}{2}u^2 - \alpha u\right] \times \exp\left[-\left(\frac{p^2}{2D_0} + \frac{V(q) - 2Q_V^0 q}{2D_0}\right)\right] \tag{73}$$

with $V(q) \approx V(0) - \frac{1}{2}\omega_b^2(q - q_b)^2$, ω_b is the barrier frequency. We now define the stationary current across the barrier as

$$j = \int_{-\infty}^{+\infty} p P_{\mathrm{St}}(q, p) dp,$$

which after using (73) gives

$$j = F_2 \exp\left(\frac{\alpha^2}{4\beta}\right) D_0\sqrt{\frac{\pi}{\beta}} \exp\left(-\frac{V(q_b)}{D_0}\right) \tag{74}$$

with $\beta = \frac{\Lambda}{2} + \frac{1}{2D_0}$. The number of particles in the left well is given by

$$n_a = \int_{-\infty}^{+\infty} dp \int_{-\infty}^{+\infty} dq\, P_{\rm St}^0(q, p)$$

where, $P_{\rm St}^0(q, p)$ (63) is the steady-state solution of the Fokker-Planck equation (61) near the bottom of the left well of the same. With the harmonic approximation near the bottom of the left well, $V(0) \approx \frac{1}{2}\omega_0^2 q^2$ at $q \approx 0$, n_a is found to be

$$n_a = F_2 \left[\sqrt{\frac{2\pi}{\Lambda}} \exp\left(\frac{\alpha^2 + Q_V^{0^2}}{2\pi} \right) + \frac{Q_V^{0^2}}{4\omega_0^2} \right] \left[1 - \Phi\left(\frac{\alpha}{2\pi} \right) \right] \left(\frac{2\pi D_0}{\omega_0} \right) \tag{75}$$

Using the definition of flux-over-population, $k = \frac{j}{n_a}$ and using (74) and (75), we get the required expression for the stationary rate, k in the Markovian limit:

$$k = \frac{\omega_0}{2\pi \left[1 - \Phi\left(\frac{\alpha}{2\pi} \right) \right]} \sqrt{\frac{\Lambda}{2\beta}} \exp\left[\alpha^2 \left(\frac{1}{4\beta} - \frac{1}{2\Lambda} \right) \right] \exp\left(-\frac{Q_V^{0^2}}{4\omega_0^2} \right) \exp\left(-\frac{V_b}{D_0} \right) \tag{76}$$

The above equation for stationary rate can be written more explicitly using the definitions of various parameters as

$$\begin{aligned} k &= \frac{\omega_0}{2\pi \left[1 - \Phi\left(\frac{\alpha}{2\pi} \right) \right]} \sqrt{\frac{\lambda}{(\lambda + \gamma)}} \\ &\quad \times \exp\left[-\frac{Q_V^{0^2}}{2} \left(\frac{\gamma}{\lambda(\lambda + \gamma)} + \frac{1}{2\omega_0^2} \right) \right] \exp\left(-\frac{V_b \gamma}{D_0} \right) \\ &= \frac{\omega_0}{2\pi \left[1 - \Phi\left(\frac{\alpha}{2\pi} \right) \right] \omega_b} \left[\sqrt{\left(\frac{\gamma}{2} \right)^2 + \omega_b^2} - \left(\frac{\gamma}{2} \right) \right] \\ &\quad \times \exp\left[-\frac{Q_V^{0^2}}{2} \left(\frac{2\gamma}{\gamma + \sqrt{\gamma^2 + 4\omega_b^2}} + \frac{1}{2\omega_0^2} \right) \right] \exp\left(-\frac{V_b \gamma}{D_0} \right) \end{aligned} \tag{77}$$

with

$$D_0 = \frac{\gamma}{2} \hbar \Omega_0 \left[\overline{n}(\Omega_0) + \frac{1}{2} \right] \tag{78a}$$

$$Q_V^0 = -\frac{1}{2} V'''(q) \langle \delta \hat{x}^2 \rangle_{\rm eq} = A \langle \delta \hat{x}^2 \rangle_{\rm eq} \tag{78b}$$

$$= \frac{A\hbar}{2\omega_0} \coth\left(\frac{\hbar \omega_0}{2\pi k_B T} \right) \tag{78c}$$

Equation (77) is the key result of our development which quantifies the characteristic quantum decay rate from a meta-stable state for a particle subjected to quantum fluctuations. The quantity D_0 in (77) is the quantum mechanical analogue of the thermal quantity $k_B T$. D_0 contains the information of pure thermal fluctuations and fluctuations due to non-linearity of the system potential which are pure quantum mechanical in nature. In the zero

temperature limit when the quantum fluctuation play the major role, (77) gives the pure tunnelling rate.

The classical Kramers' expression for rate, may be obtained if one proceeds in the following manner. In the limit of high temperature, the quantum correction terms are insignificant and the thermal fluctuations play a dominant role. Under these circumstances, (77) yields the classical rate for the thermal noise, with the underlying noise being essentially Markovian. It is quite evident from the very mode of development that we have presented here that in the absence of quantum dispersion, the term $Q_V(q,t)[= V'(q) - \langle V'(x,t)\rangle]$ vanishes, and as the classical limit (i.e. $k_BT \gg \hbar\Omega_0$) is being approached D_0 reduces to γk_BT. This obviates the vanishing of the parameters $\alpha = \frac{Q_V^0}{D_0}$, a signature of the absence of any quantum dispersion. Consequently $\Phi(\frac{\alpha}{2\pi})$ too goes off to zero. Thus, (77) provides the classical rate for thermal noise when the underlying noise processes are Markovian and one obtains the celebrated Kramers' result (corresponding classical counterpart)

$$k = \frac{\omega_0}{2\pi\omega_b}\left[\sqrt{\left(\frac{\gamma}{2}\right)^2 + \omega_b^2} - \left(\frac{\gamma}{2}\right)\right]\exp\left(-\frac{V_b}{k_BT}\right) \tag{79}$$

It is pertinent to mention here that in the usual Kramer's theory, the original non-linear potential in which the Brownian particle moves is linearized both at the bottom and the top of the potential but it has been pointed out that the quantum effects are entangled with the non-linearity of the potential. So, to study the quantum effect of escape dynamics, the non-linearity of the potential must be considered, which has been reflected through the term Q_V^0 (see (78c)), where the parameter A comes from the non-linearity of the classical potential.

In this part we will indicate the relationship of the present method with other allied method(s) in vogue. The problem of quantum mechanics for macroscopic systems has simulated considerable interest in the last few decades and the quantum version of the Kramers' problem, namely the tunnelling decay of a metastable state in the presence of coupling to a thermal bath (dissipation) has become very popular [39]. Quantum mechanical corrections to classical reaction rate were introduced first by Wigner [40] when discussing the thermal averaged transmission coefficients for parabolic barrier. The interest was stimulated by an increasing amount of experimental data that span a large temperature domain from a few mK, where quantum effects are extremely important to high temperatures at which the system can be described classically [18].

Generally, the quantum Kramers's problem is formulated by replacing the generalized Langevin equation with an equivalent Hamiltonian in which the system is coupled linearly to a bath of harmonic oscillators. Initial work on the quantum problem was implicitly based on the assumption of thermal equilibrium within the well, allowing the use of equilibrium statistical mechanics. Using a path integral approach Calderia and Leggett [17] have shown that a zero temperature dissipation leads to an exponential reduction of the tunnelling. At $T = 0$, the equilibrium assumption is valid for arbitrary coupling strength. The coupling to the thermal bath leads to an exponential enhancement of the rate at low temperature compared to its zero temperature value as shown by Larkin and Ovchinikov [41] and by Grabert, Weiss and Hänggi [42]. The above mentioned calculations are based on a thermodynamic method for the calculation of transition rates. In this approach pioneered by Langer [43] one determines the free energy of an unstable system by means of an analytical continuation and extracts the transition rate from the imaginary part. In an article Grabert et al. [44] summarized the analytical and numerical results on imaginary free energy calculations for the dissipative metastable systems. The method was found to be very successful in explaining experimental data, but its validity is not known exactly due to the lack of first principle

derivation. Ankerhold et al. [45] studied the real time dynamics of a dissipative quantum system with a potential barrier and an evolution for the time dependent density matrix was derived by employing a general framework provided by a path integral description. The quantum theory of reaction rate is almost as old as quantum mechanics itself. But even today, it presents some formidable challenge. Since the past few decades one can broadly identify two approaches. One is to recognize the difficulty in obtaining exact quantum result and proceed to find the numerically exact quantum rate. This approach has seen dramatic advances and one can now routinely obtain numerically exact rates. A second approach, especially important for the condensed matter community is to replace rigor with reasonable approximations. A strategy that has gained much popularity in recent years is to estimate quantum rate using centroid density [18]. Since a centroid density is a thermodynamic object, it can readily be estimated using Monte Carlo path integral techniques.

Although a number of interesting approaches to quantum theory of dissipative rate process based on dynamical semigroup method for evolution of density operator were proposed [1, 2] in the seventies to treat the quantum and nonlinear optical phenomena with considerable success, the method could not gain strong ground in the theory of rate process due to the fact that it is based on a weak system-reservoir coupling. The method which received major impetus afterwards in the eighties and nineties in the wide community of chemical physics is the real time functional integral. The method has been shown to be most effective in treating quantum transition states, dissipative coherent quantum effects, as well as the incoherent quantum tunnelling process [39]. Notwithstanding its phenomenal success, it may, however, be noted that compared to classical Kramers' theory, the method of functional integrals for calculation of escape rate rests on a fundamentally different footing. While the classical theory is based on the differential equation for evolution of probability distribution function of a particle executing Brownian motion in a forced field, path integral methods rely on the time evolution of quantum partition function of the system interacting with a bath of harmonic oscillators with a characteristic frequency distribution. Here, instead of path integral approach, we consider the quantum Langevin equation and obtain the corresponding c-number Langevin equation but keeping the full quantum effect in the dynamics. Then the corresponding Fokker-Planck equation is constructed to obtain the barrier crossing dynamics. It is clear from the very mode of our development that we treat the barrier crossing dynamics of a quantum system on a footing that is completely different from that of the path integral approach.

To this end, we conclude that (20) can be considered as the classical analogue of generalized Langevin equation.

6 Conclusion

Quantum systems coupled to a heat-bath environment have been found almost everywhere in physics and chemistry. What one aims to describe in this context is the effective dynamics of the relevant system degrees of freedom, that is, the reduced dynamics. While the corresponding classical theory is well established and based on Fokker-Planck equation, the formulation of quantum mechanics is more complicated. In general, a simple time evolution equation for the reduced density matrix does not exist, though the influence functional can be exactly reproduced through stochastic averaging of a process, and the formulation of which has been found to be effective for weak to moderate friction: a regime which lies beyond the validity of Redfield equations and hence beyond the applicability of Monte Carlo schemes. Furthermore, the problem of convergence of the stochastic averaging is still unsolved for a

relatively long time. Recently, starting from an initial coherent state representation and using Wigner thermal distribution for harmonic oscillator, Ray and his group have developed a c-number equation which includes the quantum correction terms. These correction terms appear as a coupled and infinite set of hierarchy of equations and for practical purposes, must be truncated after the desired order and thus can not be cast in a closed form. In our present work, based on a systematic perturbation technique we derive the quantum correction terms in a closed analytical form and in the case of an Ohmic dissipative bath, we derive the lowest order quantum correction factor exactly. Calculation of this correction factor leads us to handle the quantum dynamics in terms of the effective classical Langevin equation and hence in the framework of classical Fokker-Plank description. As an application of our methodology, including these correction terms in Fokker-Planck equation we study the barrier crossing dynamics to obtain the inverse of mean first passage time in closed form, which in the limit $k_T \gg \hbar\Omega_0$ reduces to the classical Kramers' equation. Not only barrier crossing or hopping phenomena our development can also be used to study the quantum resonance phenomena exactly. In our future work, we intend to study the stochastic resonance in quantum domain and also the zero temperature case to calculate the pure tunnelling effect and vibrational relaxation spectroscopy. Calculation of quantum correction factor for non-Ohmic bath and for non-Markovian process is also an interesting venture for further study.

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