Approach to quantum Kramers' equation and barrier crossing dynamics

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We have presented a simple approach to quantum theory of Brownian motion and barrier crossing dynamics. Based on an initial coherent state representation of bath oscillators and an equilibrium canonical distribution of quantum-mechanical mean values of their co-ordinates and momenta we have derived a *c* number generalized quantum Langevin equation. The approach allows us to implement the method of classical non-Markovian Brownian motion to realize an exact generalized non-Markovian quantum Kramers' equation. The equation is valid for arbitrary temperature and friction. We have solved this equation in the spatial diffusion-limited regime to derive quantum Kramers' rate of barrier crossing and analyze its variation as a function of the temperature and friction. While almost all the earlier theories rest on quasiprobability distribution functions (e.g., Wigner function) and path integral methods, the present work is based on *true probability distribution functions* and is independent of path integral techniques. The theory is a natural extension of the classical theory to quantum domain and provides a unified description of thermally activated processes and tunneling.

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I. INTRODUCTION

Ever since Kramers [1] reported his seminal work on the Brownian motion in phase space, the theory of noise-induced escape from metastable states has become a central issue in several areas of physical and chemical sciences. The escape is governed by Brownian motion in addition to the characteristic dynamical motion of the system in presence of a potential $V(X)$, Brownian motion being due to the thermal forces, which in turn are associated with the dissipation through fluctuation-dissipation relation at a finite temperature T. The problem and many of its variants have been addressed by a large number of workers over the last several decades at various levels of description and have been extended to semiclassical and quantum domains [1–14]. A major impetus in the development of quantum theory of dissipative processes was the discovery of laser in 1960s followed by significant advancement in the field of nonlinear and quantum optics in 1970s and 1980s when the extensive applications of nonequilibrium quantum-statistical methods were made [15,16]. Various nonlinear optical processes and phenomena were described with the help of operator Langevin equations, density operator methods, and the associated quasiclassical distribution functions. However, these dynamical semigroup methods of quantum optics could not gain much ground in the theory of activated rate processes due to the fact that these are primarily based on system-reservoir weak coupling and Markov approximations [15], which are often too drastic in the situations pertaining to chemical dynamics and condensed matter physics. Subsequent to these developments, quantum Brownian motion [2,4,5,17–22] emerged as a subject of renewed interest in early 1980s when the problem of dissipative quantum tunneling was addressed by Leggett and others and almost simultaneously quantum Kramers' problem and some allied issues attracted serious attention of a number of physical chemists. We refer to [2,3,23] for an overview.

The aforesaid development of the quantum theory of Brownian motion essentially rests on the method of functional integrals [20]. This is based on the calculation of the partition function for the Hamiltonian of the system coupled to its environment and a noncanonical quantization procedure. The classical theories on the other hand rely on the partial differential equations describing the evolution of the probability distribution functions of the system both in the Markovian and non-Markovian regions [1,3,24–27]. The methods of the classical and the quantum theories are thus widely different in their approaches. The question is whether there is any natural extension of the classical theory to the quantum domain. For example, one might ask what is the quantum analog of the classical Kramers' equation or Smoluchowskii's equation? Is it possible to generalize Kramers' method of treatment of barrier crossing dynamics within a quantum-mechanical framework so that the usual classical thermal activated process and quantum tunneling can be described within an unified scheme?

We intend to address these issues in the present paper. Specifically our object is twofold.

(1) Our primary aim here is to develop a *quantum analog of classical non-Markovian Kramers' equation,* which describes quantum Brownian motion of a particle in a force field at an arbitrary temperature and coupling in terms of *true probability distribution* function rather than quasiprobability function [28,29]. The generalized quantum Kramers' equation (GQKE) reduces to its classical counterpart in the limit $h\rightarrow 0$ both in Markovian and non-Markovian descriptions. The probability distribution functions remain well behaved in the full quantum limit.

(2) While the existing methods of calculation of quantum Kramers' rate are based on path integral techniques, we solve GQKE for barrier crossing dynamics as a boundary value problem taking care of the full quantum nature of the system and the bath. The generalized rate in the spatial diffusion-limited regime reduces to Kramers-Grote-Hynes' rate in the classical limit and to pure tunneling rate in the quantum limit at zero temperature. To the best of our knowledge, the imple-

mentation of a differential equation based approach, as the present one, has not been tried till data for a full quantum-mechanical calculation of the rate.

Based on an initial coherent state representation of the bath oscillators and an equilibrium canonical distribution of the quantum-mechanical mean values of their co-ordinates and momenta, we derive a generalized quantum Langevin equation in *c* numbers. The bath imparts classical looking *c* number quantum noise, which satisfies standard fluctuation-dissipation relation. The simplicity of the treatment lies in the fact that the quantum Langevin equation is amenable to a theoretical analysis in terms of the well known classical non-Markovian theory of Brownian motion [24,25] so that the GQKE assumes the form of its classical counterpart. In what follows we show that GQKE can be solved in the spirit of Kramers' method to calculate the quantum escape rate. This recasting of the quantum problem into a classical form allows us to realize the various limits of the theory on a general footing.

The organization of the paper is as follows. We introduce the system-reservoir model and an ensemble averaging procedure to derive the generalized quantum Langevin equation in a *c* number form in the following section. In Sec. III we derive the corresponding GQKE followed by a calculation of quantum rate of escape in Sec. IV. The key result is illustrated in Sec. V by assuming a Lorentzian density distribution of bath oscillators and a specific cubic potential. The paper is concluded in Sec. VI.

II. THE GENERALIZED QUANTUM LANGEVIN EQUATION IN *C* NUMBERS

To start with we consider the standard system heat bath model of Zwanzig form [30]. The Hamiltonian is given by

$$\hat{H}=\frac{\hat{P}^2}{2}+V(\hat{X})+\sum_j\left[\frac{\hat{p}_j^2}{2}+\frac{1}{2}\kappa_j(\hat{q}_j-\hat{X})^2\right]. \tag{1}$$

Here $\hat{X}$ and $\dot{P}$ are the co-ordinate and momentum operators of the Brownian particle (the system) of unit mass and the set $\{\hat{q}_j,\hat{p}_j\}$ is the set of co-ordinate and momentum operators for the heat bath particles. The mass of the jth particle is unity and κ_j is the spring constant of the spring connecting it to the Brownian particle. The potential $V(\hat{X})$ is due to the external force field for the Brownian particle. The co-ordinate and momentum operators follow the usual commutation relations

$$[\hat{X},\hat{P}]=i\hbar \quad \text{and} \quad [\hat{q}_j,\hat{p}_j]=i\hbar\,\delta_{ij} \tag{2}$$

Eliminating the bath degrees of freedom in the usual way [15,31] we obtain the operator Langevin equation for the particle

$$\ddot{\hat{X}}+\int_0^1 dt'\,\beta(t-t')\dot{\hat{X}}(t')+V'(\hat{X})=\hat{F}(t) \tag{3}$$

where the noise operator $\hat{F}(t)$ and memory kernel $\beta(t)$ are given by

$$\hat{F}(t)=\sum_j\ |\{\hat{q}_1(0)-\hat{X}(0)\}\kappa_j\cos\omega_j t+\hat{p}_j(0)\kappa_j^{1/2}\sin\omega_j t|. \tag{4}$$

and

$$\beta(t)=\sum_j\ \kappa_j\cos\omega_j t, \tag{5}$$

where $\omega_j^2=\kappa_j$ and the initial variations of the heat bath variables $\hat{q}_j(0)$ and $\hat{p}_j(0)$ occur in the force term $\hat{F}(t)$. The relevant quantum-statistical averages are well known

$$\langle\hat{F}\rangle_{\rm QS}=0 \tag{6}$$

and

$$\tfrac{1}{2}[\langle\hat{F}(t')\hat{F}(t)\rangle_{\rm QS}+\langle\hat{F}(t)\hat{F}(t')\rangle_{\rm QS}] =\frac{1}{2}\sum_j\ \kappa_j\hbar\omega_j\left(\coth\frac{\hbar\omega j}{2k_bT}\right)\cos\omega_j(t-t'). \tag{7}$$

Here $\langle\cdots\rangle_{\rm QS}$ refers to quantum-statistical average on the bath degrees of freedom. To arrive at the above relations, one assumes [31] that the bath oscillators are canonically distributed with respect to the bath Hamiltonian at $t=0$ so that for any operator $\hat{O}$ the average is

$$\langle\hat{O}\rangle_{\rm QS}=\frac{{\rm Tr}\hat{O}\exp(-\hat{H}_{\rm bath}/k_BT)}{{\rm Tr}\exp(-\hat{H}_{\rm bath}/k_BT)} \tag{8}$$

where $\hat{H}_{\rm bath}=\Sigma_j[(\hat{p}_j^2/2)+(1/2)\kappa_j(\hat{q}_j-\hat{X})^2]$ By trace we mean carrying out quantum-statistical average with number states of the bath oscillators multiplied by the arbitrary state of the particle. Equation (7) is the celebrated fluctuation-dissipation relation (FDR).

Equation (3) is an exact quantum Langevin equation in operator form, which is a standard textbook material [15,31]. Our aim here is to replace it by an equivalent quantum generalized Langevin equation (QGLE) in *c* numbers. It is important to mention here that again this is not a new problem [15,16] so long as one is restricted to standard quasiclassical methods of Wigner functions and the like. In general, however, one is confronted with serious trouble of negativity or singularity of these quasiprobability distribution functions in the full quantum domain. To address the problem of quantum non-Markovian dynamics in terms of a *true probabilistic description* we, however, follow a different procedure. Our approach here is to split up the quantum-statistical averaging procedure in *two distinct* steps. We *first* carry out the quantum-mechanical average of Eq. (3)

$$\langle\ddot{\hat{X}}\rangle+\langle V'(X)\rangle+\int_0^t\beta(t-t')\langle\dot{\hat{X}}(t')\rangle dt'=\langle\hat{F}(t)\rangle, \tag{9}$$

where the averaging is taken over the initial product separable quantum states of the particle and the bath oscillators at $t=0$, $|\phi\rangle\{|\alpha_1\rangle|\alpha_2\rangle\cdots|\alpha_N\rangle\}$. Here $|\phi\rangle$ denotes any arbitrary

initial state of the particle and $|\alpha_i\rangle$ corresponds to the initial coherent state of the ith bath oscillator. $|\alpha_i\rangle$ is given by $|\alpha_i\rangle = \exp(-|\alpha_i|^2/2)\Sigma_{n_i=0}^{\infty}(\alpha_i^{n_i}/\sqrt{n_i})|n_i\rangle$, α_i is expressed in terms of the variables of the coordinate and momentum of the ith oscillator $\langle\hat{q}_i(0)\rangle = \sqrt{\hbar/(2\omega_i)}(\alpha_i+\alpha_i^*)$ and $\langle\hat{p}_j(0)\rangle = i\sqrt{\hbar\omega_i/2}(\alpha_i-\alpha_i^*)$, respectively. It is important to note that $\langle\hat{F}(t)\rangle$ of Eq. (9) is a classical-like noise term which, in general, is a nonzero number because of the averaging procedure over the coordinate and momentum operators of the bath oscillators with respect to initial coherent state and is given by

$$\langle\hat{F}(t)\rangle = \sum_j \left[\{\langle\hat{q}_j(0)\rangle - \langle\hat{X}(0)\rangle\}\kappa_j \cos w_j t + \langle\hat{p}_j(0)\rangle\kappa_j^{1/2}\sin w_j t\right] = f(t) \tag{10}$$

We now turn to the *second* averaging. To realize $f(t)$ an effective c-number noise we now demand that it must satisfy

$$\langle f(t)\rangle_s = 0$$

and

$$\langle f(t)f(t')\rangle_s = \frac{1}{2}\sum \kappa_j\hbar\omega_j\left(\coth\frac{\hbar\omega_j}{2k_bT}\right)\cos\omega_j(t-t'). \tag{11}$$

That is, $f(t)$ is zero centered and satisfies quantum fluctuation-dissipation relation. This may be achieved if and only if one introduces the following canonical distribution of quantum-mechanical mean values of the bath oscillators at $t=0$:

$$P_j = \exp\left[-\frac{|\omega_j^2\{\langle\hat{q}_j(0)\rangle - \langle\hat{X}(0)\rangle\}^2 + \langle\hat{p}_j(0)\rangle^2|}{2\hbar\omega_j(\overline{n_j}+\frac{1}{2})}\right] \tag{12}$$

so that for any quantum-mechanical mean value $O_j(\langle\hat{p}_j(0)\rangle, \{\langle\hat{q}_j(0)\rangle - \langle\hat{X}(0)\rangle\})$, the statistical average is

$$\langle O_j\rangle_S = \int O_j(\langle\hat{p}_j(0)\rangle, \{\langle\hat{q}_j(0)\rangle - \langle\hat{X}(0)\rangle\})P_j d\langle\hat{p}_j(0)\rangle d\{\langle\hat{q}_j(0)\rangle - \langle\hat{X}(0)\rangle\}. \tag{13}$$

Here $\overline{n_j}$ indicates the average thermal photon number of the jth oscillator at temperature T as defined by $\overline{n_j} = 1/[\exp(\hbar\omega_j/k_BT)-1]$.

To proceed further we now add the force term $V'(\langle\hat{X}\rangle)$ on both sides of Eq. (9) and rearrange it to obtain formally

$$\langle\ddot{\hat{X}}\rangle + V'(\langle\hat{X}\rangle) + \int_0^t \beta(t-t')\langle\dot{\hat{X}}(t')\rangle dt' = f(t) + Q(t), \tag{14}$$

where

$$Q(t) = V'(\langle\hat{X}\rangle) - \langle V'(\hat{X})\rangle \tag{15}$$

represents the quantum-mechanical dispersion of the force operator $V'(\hat{X})$ due to the system degree of freedom. Since $Q(t)$ is a quantum fluctuation term Eq. (14) offers a simple interpretation. This implies that the classical looking generalized quantum Langevin equation is governed by a c-number quantum noise $f(t)$ that originates from the quantum-mechanical heat bath characterized by the properties (11) and a quantum fluctuation term $Q(t)$ due to the quantum nature of the system characteristic of the nonlinearity of the potential. $Q(t)$ can be calculated order by order. In Appendix A we show how $Q(t)$ can be calculated in the lowest order.

Summarizing the above discussions we point out that it is possible to formulate a QGLE (14) of the quantum-mechanical mean value of the coordinate of the Brownian particle in a field of potential $V(\hat{X})$, provided a classical-like noise term $f(t)$ due to thermal bath satisfies Eq. (11) where the ensemble average has to be carried out with distribution (12). To realize $f(t)$ as a noise term we have split up the quantum-statistical averaging $\langle\cdots\rangle_{\rm QS}$ into a quantum-mechanical mean $\langle\cdots\rangle$ by the explicit use of an initial coherent state representation of the bath oscillators and then a statistical averaging $\langle\cdots\rangle_s$ of the quantum-mechanical mean values with Eq. (12). It is easy to note that the distribution of the quantum-mechanical mean values of the bath oscillators (12) reduces to classical Maxwell-Boltzmann distribution in the thermal limit $\hbar\omega_j \ll k_BT$, i.e. $\exp[-(\omega_j^2[\langle\hat{q}_j(0)\rangle - \langle\hat{X}(0)\rangle]^2 + \langle\hat{p}_j(0)\rangle^2)/2k_BT]$. Secondly, the vacuum term in the distribution (12) prevents the distribution function from being singular at $T=0$. In other words the width of distribution remains finite even at absolute zero, which is a simple consequence of uncertainty principle.

III. THE GENERALIZED QUANTUM KRAMERS' EQUATION

It is now convenient to rewrite the generalized Langevin equation (14) of the Brownian particle in presence of an external force field in the form

$$\ddot{x} + V'(x) + \int_0^t \beta(t-t')\dot{x}(t')dt' = f(t) + Q(t). \tag{16}$$

where we let $\langle\hat{X}\rangle = x$ for a simple notational change. $\beta(t)$ is the dissipative kernel and $f(t)$ is the zero-centered stationary noise due to the reservoir where

$$\langle f(t)\rangle_s = 0, \quad \langle f(t)f(t')\rangle_s = c(|t-t'|) = c(\tau). \tag{17}$$

Here $c(\tau)$ is the correlation function, which in the equilibrium state is connected to memory kernel $\beta(t)$ through FDR of the form

$$c(t-t') = \frac{1}{2}\int_0^\infty d\omega\,\kappa(\omega)\rho(\omega)\hbar\omega\left[\coth\frac{\hbar\omega}{2k_BT}\right]\cos\omega(t-t'). \tag{18}$$

Equation (18) is the continuum version of Eq. (11). $\rho(\omega)$ is the density of modes of the reservoir oscillators. In the continuum version $\beta(t)$ is given by

$$\beta(t-t')=\int_0^\infty d\omega\,\kappa(\omega)\rho(\omega)\cos\omega(t-t') \tag{19}$$

In the high temperature limit ($k_BT\gg\hbar\omega$) one recovers the well-known classical FDR through

$$c(t-t')=k_BT\beta(t-t'). \tag{20}$$

We now proceed to the solution of Eq. (16). One of the essential steps in this direction is to linearize the potential $V(x)$ in the left-hand side of Eq. (16) around the bottom of the well at $x=x_0$ so that $V(x)=V(x_0)+(\frac{1}{2})\omega_0^2(x-x_0)^2$. ω_0^2 refers to the second derivative of the potential $V(x)$ evaluated at $x=x_0$. This together with a Laplace transform of Eq. (16) leads us to the following general solution (we take $x_0=0$ for the present section):

$$x(t)=\langle x(t)\rangle_s+\int_0^t M_0(t-\tau)f(\tau)d\tau, \tag{21}$$

where

$$\langle x(t)\rangle_s=v(0)M_0(t)+x(0)\chi_x(t)+G_0(t) \tag{22}$$

and

$$G_0(t)=\int_0^t M_0(t-\tau)Q_0(\tau)d\tau. \tag{23}$$

$$\chi_x(t)=1-\omega_0^2\int_0^t M_0(\tau)d\tau \tag{24}$$

with $x(0)$ and $v(0)$ [equal to $\dot{x}(0)$] being the initial quantum-mechanical mean values of the coordinate and velocity of the particle, respectively. $M_0(t)$ is the inverse form of the Laplace transform of

$$\tilde{M}_0(s)=\frac{1}{s^2+s\tilde{\beta}(s)+\omega_0^2} \tag{25}$$

with

$$\tilde{\beta}(s)=\int_0^\infty \beta(t)e^{-st}dt \tag{26}$$

is the Laplace transform of the dissipative kernel $\beta(t)$. The subscript 0 in Q_0, M_0, and G_0 signifies that the corresponding dynamical quantities are to be calculated around $x=x_0$. The time derivative of Eq. (21) gives

$$v(t)=\langle v(t)\rangle_s+\int_0^t m_0(t-\tau)f(\tau)d\tau, \tag{27}$$

where

$$\langle v(t)\rangle_s=v(0)m_0(t)-x(0)\omega_0^2M_0(t)+g_0(t) \tag{28}$$

with

$$m_0(t)=\frac{d}{dt}M_0(t)\ \text{ and }\ g_0=\frac{d}{dt}G_0(t). \tag{29}$$

It is not difficult to check that $M_0(t)$ and $m_0(t)$ are the two relaxation functions; m_0 measures how the system with a quantum-mechanical mean velocity forgets its initial value while $M_0(t)$ concerns the relaxation of quantum-mechanical mean displacement.

Now using the symmetry properties of the correlation function $\langle f(t)f(t')\rangle_s$ [equal to $c(t-t')=c(t'-t)$] and the solution for $x(t)$ and $v(t)$ from Eqs. (21) and (27) we obtain the following expressions for the variances:

$$\sigma_{xx}^2(t)=\langle[x(t)-\langle x(t)\rangle_s]^2\rangle_s$$

$$=2\int_0^t M_0(t_1)dt_1\int_0^{t_1}M_0(t_2)c(t_1-t_2)dt_2 \tag{30a}$$

$$\sigma_{vv}^2(t)=\langle[v(t)-\langle v(t)\rangle_s]^2\rangle_s$$

$$=2\int_0^t m_0(t_1)dt_1\int_0^{t_1}m_0(t_2)c(t_1-t_2)dt_2 \tag{30b}$$

$$\sigma_{xv}^2(t)=\langle[x(t)-\langle x(t)\rangle_s][v(t)-\langle v(t)\rangle_s]\rangle_s=\tfrac{1}{2}\dot{\sigma}_{xx}(t)$$

$$=\int_0^t M_0(t_1)dt_1\int_0^{t_1}m_0(t_2)c(t_1-t_2)dt_2. \tag{30c}$$

The expressions for variances are general and valid for arbitrary temperature and friction and includes quantum effects. To recover classical limit of the variances $\sigma_{xv}^2(t),\sigma_{vv}^2(t),\sigma_{xv}^2(t)$ one has to use Eq. (20) instead of Eq. (18) in Eqs. (30a)–(30c). It must also be emphasized that Eqs. (30a)–(30c) are the expressions for statistical variances of the quantum-mechanical mean values $x(t)$ and $v(t)$ with distribution (12). These are not to be confused with standard quantum-mechanical variances, which are connected through the uncertainty relation.

Having obtained the expressions for statistical averages and variances we are now in a position to write down the quantum Kramers equation, which is a Fokker-Planck description for the evolution of true probability density function $p(x,v,t)$ of the quantum-mechanical mean values of the co-ordinate and momentum of the particle. To this end it is necessary to consider the statistical distribution of noise $f(t)$, which we assume here to be Gaussian. For Gaussian noise processes we define [25,31,34] the joint characteristic function $\overline{p}(\mu,\rho,t)$ in terms of the standard mean values and variances

$$\tilde{p}(\mu,p,t)=\exp[i\mu\langle x(t)\rangle_s+i\rho\langle v(t)\rangle_s-\tfrac{1}{2}\{\sigma_{xx}^2\mu^2+2\sigma_{xv}^2\rho\mu+\sigma_{vv}^2\rho^2\}] \tag{31}$$

Using standard procedure [24,25,31,34] we write down the quantum Kramers' equation obeyed by the joint probabil-

ity distribution $p(x,v,t)$, which is the inverse Fourier transform of the characteristic function

$$\frac{\partial p(x,v,t)}{\partial t}=\left\{-v\frac{\partial}{\partial x}+\tilde{V}'(x)\frac{\partial}{\partial v}+[\Omega_0(t)-N_0(t))\frac{\partial}{\partial v}\right\}p(x,v,t)+\left\{g_0(t)\frac{\partial}{\partial x}+\tilde{\gamma}_0(t)\frac{\partial}{\partial v}v+\phi_0(t)\frac{\partial^2}{\partial v^2}+\psi_0(t)\frac{\partial^2}{\partial v\,\partial x}\right\}p(x,v,t), \tag{32}$$

where

$$g_0(t)=\dot{G}_0(t), \tag{33a}$$

$$\tilde{\gamma}_0(t)=-\frac{d}{dt}[\ln Y_0(t)], \tag{33b}$$

$$Y_0(t)=\frac{m_0(t)}{\omega_0^2}\left[1-\omega_0^2\int_0^t M_0(\tau)d\tau\right]+M_0^2(t), \tag{33c}$$

$$\tilde{\omega}_0^2(t)=\frac{1}{Y_0(t)}[-M_0(t)\dot{m}_0(t)+m_0^2(t)], \tag{33d}$$

$$N_0(t)=\frac{1}{Y_0(t)}\left[-g_0(t)\dot{m}_0\frac{1}{\omega_0^2}\left(1-\omega_0^2\int_0^t M_0(t)d\tau\right)+m_0^2G_0\right] \tag{33e}$$

$$\Omega_0(t)=M_0(t)\frac{d}{dt}[G_0(t)m_0(t)] \tag{33f}$$

$$\phi_0(t)=\tilde{\omega}_0^2(t)\sigma_{xv}^2(t)+\tilde{\gamma}_0(t)\sigma_{vv}^2(t)+\tfrac{1}{2}\dot{\sigma}_{vv}^2(t) \tag{33g}$$

$$\psi_0(t)=\dot{\sigma}_{xv}^2(t)+\tilde{\gamma}_0(t)\sigma_{xv}^2(t)+\tilde{\omega}_0^2(t)\sigma_{xx}^2(t)-\sigma_{vv}^2(t). \tag{33h}$$

$\tilde{V}(x)$ is the renormalized potential linearized at the bottom of the well at $x=0$, the frequency being $\tilde{\omega}_0(t)$ as given by Eq. (33d). The above Kramers' equation (32) is the quantum-mechanical version of the classical non-Markovian Kramers equation and is valid for arbitrary temperature and friction. The quantum effects appear in the description in two different ways. First, due to the explicit Q dependence $g_0(t)$ [see Eqs. (23) and (33a)], $\Omega_0(t)$ and $N_0(t)$ manifestly include the effect of quantum dispersion of the system through the nonlinearity of the potential. Second, the quantum diffusion coefficients $\phi_0(t)$ and $\psi_0(t)$ are due to the quantum-mechanical heat reservoir. In the classical limit $g_0(t),\Omega_0(t),N_0(t)$ vanishes while $\dot{\phi}_0(t)$ and $\psi_0(t)$ reduce to the forms that can be obtained by using the classical fluctuation-dissipation relation (20) in Eq. (30) and Eqs. (33g) and (33h). In the classical limit $k_BT\gg\hbar\omega$ Eq. (32) therefore reduces exactly to non-Markovian Kramers' equation derived earlier by Adelman and Mazo in late 1970s [24,25].

It is important to emphasize that Eq. (32) retains its full validity in the quantum limit when $T\to 0$. It is also apparent that G_0 in Eq. (23) [therefore in $g_0(t)$] demonstrates a direct convolution of the relaxation function $M_0(t)$ with quantum dispersion $Q_0(t)$. This is a clear signature of the interplay of dissipation with the nonlinearity of the potential within a quantum description.

The decisive advantage of the present approach is noteworthy. We have mapped the operator generalized Langevin equation (3) into a generalized equation for c numbers (16) and a corresponding non-Markovian Kramers' equation (32). The present approach thus bypasses the earlier methods of quasiprobability distribution functions employed widely in quantum optics over the decades in a number of ways. First unlike the *quasiprobability* distribution function, the probability distribution function $p(x,v,t)$ is valid for non-Markovian processes. Second, while the corresponding characteristic functions for probability distribution functions are operators, we make use of the classical characteristic functions. Third, as pointed out earlier the quasidistribution functions often become negative or singular in the strong quantum domain and pose serious problems [15,32]. The present approach is free from such shortcomings since $p(x,v,t)$ is a *true probability distribution* function rather than a *quasiprobability* function [28,29]. Fourth, the generalized quantum Kramers' equation derived here is valid for arbitrary temperature and friction.

Regarding quantum generalized Kramers' equation we further note that although bounded, the time dependent functions $\tilde{\gamma}_0(t),\phi_0(t),\psi_0(t)$ may not always provide the long time limits. This is well known in classical theories [24,25]. These play an important role in the calculation of non-Markovian Kramers' rate. Therefore, in general, one has to work out the frequency $\tilde{\omega}_0(t)$ and friction $\tilde{\gamma}_0(t)$ functions for the analytically tractable models. In Sec. V we shall consider one such explicit example.

We now consider the stationary distribution of the particles near $x=0$ that can be expressed as a solution of Eq. (32) for $\partial p_{st}^0/\partial t=0$

$$\left\{v\frac{\partial}{\partial x}-g_0(\infty)\frac{\partial}{\partial x}-\tilde{\omega}_0^2(\infty)x\frac{\partial}{\partial v}-[\Omega_0(\infty)-N_0(\infty)]\frac{\partial}{\partial v}\right\}p_{st}^0(x,v)-\left\{\tilde{\gamma}_0(\infty)\frac{\partial}{\partial v}v+\phi_0(\infty)\frac{\partial^2}{\partial v^2}+\psi_0(\infty)\frac{\partial^2}{\partial v\,\partial x}\right\}p_{st}^0(x,v)=0. \tag{34}$$

where the drift and diffusion coefficients of Eq. (34) assume their asymptotic values.

It may be checked immediately that the stationary solution of Eq. (34) is given by

$$p_{st}^0(x,v)=\frac{1}{Z}\exp\left[-\frac{(v-g_0)^2}{2D_0}\right]\times\exp\left[-\frac{\tilde{V}(x)+x(\Omega_0-N_0+\tilde{\gamma}_0g_0)}{D_0+\psi_0}\right]. \tag{35}$$

where $D_0=\phi_0(\infty)/\tilde{\gamma}_0(\infty)$; ψ_0, ϕ_0, Ω_0, N_0 and g_0 are the values of the corresponding quantities in the long time limit. Z is the normalization constant. Here $\tilde{V}(x)$ is the renormalized linear potential with a renormalization in its frequency.

Equation (35) is the quantum steady state distribution. It may be checked easily that in the classical Markovian limit the ratio D_0 goes over to k_BT while ψ_0 vanishes along with g_0,Ω_0,N_0 reducing Eq. (35) to the form of Maxwell-Boltzmann distribution function. In what follows in the next section we shall make use of the quantum distribution (35) as a boundary condition for calculation of Kramers' rate.

IV. THE QUANTUM KRAMERS' RATE

We now turn to the problem of barrier crossing dynamics. In Kramers' approach the particle coordinate x (which in our case it is the quantum-mechanical mean position) corresponds to the reaction co-ordinate and its values at the minima of $V(x)$ denotes the reactant and the product states separated by a finite barrier, the top being a metastable state representing the transition state.

Linearizing the motion around the barrier top at $x=x_b$ the Langevin equation can be written down as

$$\ddot{x}-\omega_b^2(x-x_b)+\int_0^t\beta(t-t')\dot{x}(t')dt'=f(t)+Q_b(t), \tag{36}$$

where the barrier frequency ω_b^2 is defined by $V(x)=V(x_b)-(\frac{1}{2})\omega_b^2(x-x_b)^2$. Also the quantum dispersion Q_b has to be calculated at the barrier top. Correspondingly the motion of the quantum particle is governed by the Fokker-Planck equation

$$\frac{\partial p(x,v,t)}{\partial t}=-\left\{v\frac{\partial}{\partial x}-g_b(t)\frac{\partial}{\partial x}+\tilde{\omega}_b^2(x-x_b)\frac{\partial}{\partial v}-[\Omega_b(t)-N_b(t)]\frac{\partial}{\partial v}\right\}p(x,v,t)+\left\{\tilde{\gamma}_b(t)\frac{\partial}{\partial v}v+\phi_b(t)\frac{\partial^2}{\partial v^2}+\psi_b(t)\frac{\partial^2}{\partial v\,\partial x}\right\}p(x,v,t). \tag{37}$$

where the subscript 'b' indicates that all the coefficients are to be calculated at the barrier top using the general definition of the last section where

$$\tilde{M}_b(s)=\frac{1}{s^2+s\overline{\beta}(s)-\omega_b^2}, \tag{38}$$

which is the Laplace transform of $M_b(t)$ and

$$\chi_x^b(t)=1+\omega_b^2\int_0^t M_b(t')dt^t. \tag{39a}$$

Furthermore we have

$$m_b=\dot{M}_b \text{ and } g_b(t)=\dot{G}_b(t); \tag{39b}$$

$$\tilde{\gamma}_b(t)=-\frac{d}{dt}[\ln Y_b(t)], \tag{40a}$$

$$Y_b(t)=\frac{m_b(t)}{\omega_b^2}\left[1+\omega_b^2\int_0^t M_b(\tau)dr\right]+M_b^2(t), \tag{40b}$$

$$\tilde{\omega}_b^2(t)=\frac{1}{Y_b(t)}[-M_b(t)\dot{m}_b(t)+m_b^2(t)], \tag{40c}$$

$$N_b(t)=\frac{1}{Y_b(t)}\left[g_b(t)\dot{m}_b\frac{1}{\omega_b^2}\left(1+\omega_b^2\int_0^t M_b(\tau)d\tau\right)+m_b^2G_b\right], \tag{40d}$$

$$\Omega_b(t)=M_b(t)\frac{d}{dt}[G_b(t)m_b(t)], \tag{40e}$$

$$\phi_b(t)=\tilde{\omega}_b^2(t)\sigma_{xv}^2(t)+\tilde{\gamma}_0(t)\sigma_{vv}^2(t)+\tfrac{1}{2}\dot{\sigma}_{vv}^2(t), \tag{40f}$$

$$\psi_b(t)=\dot{\sigma}_{xv}^2(t)+\tilde{\gamma}_b(t)\sigma_{xv}^2(t)+\tilde{\omega}_b^2(t)\sigma_{xx}^2(t)-\sigma_{vv}^2(t), \tag{40g}$$

In the spirit of classical Kramers' ansatz [1] we now demand a solution of Eq. (37) at the stationary limit of the type

$$p_{st}(x,v)=p_0(x,v)\zeta(x,v), \tag{41}$$

with

$$p_0(x,v)=\exp\left[-\frac{(v-g_b)^2}{2D_b}-\frac{\tilde{V}(x)+x(\Omega_b-N_b+\tilde{\gamma}_bg_b)}{D_b+\psi_b}\right] \tag{42}$$

where $D_b=\phi_b(\infty)/\tilde{\gamma}_b(\infty)$; ψ_b, g_b, N_b, $\tilde{\gamma}_b$ are the long time limits of the corresponding time dependent quantities specific for the barrier region. The exponential factor in Eq. (41) is not the Boltzmann distribution but pertains to the dynamics at the barrier top at $x=x_b$. Due to the presence of g_b, Ω_b, N_b one may easily comprehend the signature of quantum nature of the system while ϕ_b, ψ_b carries the effect of quantum noise due to heat bath. The distribution p_0 remains finite even at absolute zero.

Now inserting Eq. (41), in Eq. (37) in the steady state we obtain

$$-\left(1+\frac{\psi_b}{D_b}\right)(v-g_b)\frac{\partial\zeta}{\partial x}-\left[\frac{D_b}{\psi_b+D_b}\tilde{\omega}_b^2\times\left(x-x_b-\frac{(\Omega_b-N_b)-\tilde{\gamma}_bg_b}{\tilde{\omega}_b^2}\right)+\tilde{\gamma}_b(v-g_b)\right]\frac{\partial\zeta}{\partial v}+\phi_b\frac{\partial^2\zeta}{\partial v^2}+\psi_b\frac{\partial^2\zeta}{\partial x\,\partial v}=0. \tag{43}$$

We then set

$$u=a(x+\alpha_b)+v-g_b, \tag{44}$$

where

$$\alpha_b = -\left[\frac{\Omega_b - N_b + \tilde{\gamma}_b g_b + x_b \tilde{\omega}_b}{\tilde{\omega}_b^2}\right]. \tag{45}$$

and with the help of transformation (44) Eq. (43) is reduced to the following form:

$$(\phi_b + a\psi_b)\frac{\partial^2 \zeta}{\partial u^2} - \left[\frac{D_b}{\psi_b + D_b}\tilde{\omega}_b^2 (x+\alpha_b) + \left\{\tilde{\gamma}_b + a\left(1 + \frac{\psi_b}{D_b}\right)\right\} \times (v - g_b)\right]\frac{\partial \zeta}{\partial u} = 0. \tag{46}$$

Now let

$$\frac{D_b}{\psi_b + D_b}\tilde{\omega}_b^2 (x + a_b) + \left\{\tilde{\gamma}_b + a\left(1 + \frac{\psi_b}{D_b}\right)\right\}(v - g_b) = \lambda u, \tag{47}$$

where λ is a constant to be determined.

From Eqs. (44) and (47) we obtain

$$a_{\pm} = -\frac{B}{2A} \pm \sqrt{(B^2/4A) + (C/A)}, \tag{48}$$

where

$$A = 1 + \frac{\psi_b}{D_b}, \quad B = \tilde{\gamma}_b, \quad \text{and} \quad C = \frac{D_b}{\psi_b + D_b} - \tilde{\omega}_b^2 \tag{49}$$

By virtue of the relation (47), Eq. (46) becomes

$$\frac{d^2 \zeta}{du^2} + \Lambda u \frac{d\zeta}{du} = 0, \tag{50}$$

where

$$\Lambda = \left[\frac{\lambda}{\phi_b + a\psi_b}\right]. \tag{51}$$

The general solution of the homogeneous differential equation (50) is

$$\zeta(u) = F_2 \int_0^u \exp\left(-\frac{\Lambda u^2}{2}\right) du + F_1 \tag{52}$$

where F_1 and F_2 are the two constants of integration.

The integral in Eq. (52) converges for $|u| \to \infty$ if only Λ is positive. The positivity of Λ depends on the sign of a; so by virtue of Eqs. (44) and (47) we find that the negative root of a. i.e., a guarantees the positivity of Λ since $-\lambda a = C$. To determine the value of F_1 and F_2 we impose the first boundary condition on ζ

$$\zeta(x,v) \to 0 \quad \text{as} \quad x \to \infty \quad \text{for all} \quad v. \tag{53}$$

This condition yields

$$F_1 = F_2\left(\frac{\pi}{2\Lambda}\right)^{1/2} \tag{54}$$

By insertion of Eq. (54) in Eq. (52) we obtain

$$\zeta(u) = F_2\left[\left(\frac{\pi}{2\Lambda}\right)^{1/2} + \int_0^u c^{-(\Lambda^2/2)} du\right]. \tag{55}$$

Since we are to calculate the current at the barrier top, we expand the renormalized potential $\tilde{V}(x)$ around $x = x_b$

$$\tilde{V}(x) = \tilde{v}(x_b) - \tfrac{1}{2}\tilde{\omega}_b^2 (x - x_b)^2. \tag{56}$$

Thus with the help of Eqs. (55) and (56) Eq. (41) becomes

$$p_{st}(x = x_b, v) = F_2 \exp\left(-\frac{\tilde{V}(x_b) + x_b(\Omega_b - N_b + g_b\tilde{\gamma}_b)}{D_b + \psi_b}\right) \times \left[\left(\frac{\pi}{2\Lambda}\right)^{1/2} \exp\left(-\frac{(v - g_b)^2}{2D_b}\right) + F(x = x_b, v) \times \exp\left(-\frac{(v - g_b)^2}{2D_b}\right)\right] \tag{57}$$

with

$$F(x,v) = \int_0^u e^{-(\Lambda^2/2)} du. \tag{58}$$

We now, define the steady state current j across the barrier as

$$j = \int_{-\infty}^{+\infty} v\, p_{st}(x = x_b, v)\, dv. \tag{59}$$

An explicit evaluation of the integral using Eq. (57) yields the expression for current j at the barrier by

$$j = F_2\left[D_b\left(\frac{2\pi D_b}{(1 + D_b)}\right)^{1/2} \exp\left\{-\frac{\Lambda a^2 (\alpha_b + x_b)^2}{2(1 + \Lambda D_b)}\right\} + g_b\left\{\left(\frac{\pi}{2\Lambda}\right)^{1/2}\sqrt{2D_b\pi} + I\right\}\right] \times \exp\left\{-\frac{\tilde{V}(x_b) + x_b(\Omega_b - N_b + g_b\tilde{\gamma}_b)}{D_b + \psi_b}\right\}, \tag{60}$$

where

$$I = \int_{-\infty}^{+\infty} F(x = x_b, v) \exp\left[-\frac{(v - g_b)^2}{2D_b}\right] dv. \tag{61}$$

Having obtained the stationary current at the barrier top we now determine the constant F_2 in Eq. (60) in terms of the population of the left well around $x = x_0$. This may be done by matching the two appropriately reduced probability distributions at the bottom of the left well.

To this end we return to Eq. (41), which describes the steady state distribution at the barrier top. With the help of Eq. (55) we write

$$p_{st}(x,v)=F_2\exp\left[-\frac{\tilde{V}(x)+x(\Omega_b-N_b+g_b\tilde{\gamma}_b)}{D_b+\psi_b}\right]\times\exp\left[-\frac{(v-g_b)^2}{2D_b}\right]\left[\left(\frac{\pi}{2\Lambda}\right)^{1/2}+\int_0^u\exp\left(-\frac{\Lambda u^2}{2}\right)du\right]. \tag{62}$$

We first note that as $x\to\infty$, $u\to\infty$ the preexponential factor in $p_{st}(x,v)$ reduces to the form

$$F_2[\cdots]=F_2\left(\frac{2\pi}{\Lambda}\right)^{1/2}. \tag{63}$$

We now define a reduced distribution function in x as

$$\tilde{p}_{st}(x)=\int_{-\infty}^{+\infty}p_{st}(x,v)dv. \tag{64}$$

Hence from Eqs. (63) and (64) we obtain

$$\tilde{p}_{st}(x)=2\pi F_2\left(\frac{D_b}{\Lambda}\right)^{1/2}\exp\left[-\frac{\tilde{V}(x)+x(\Omega_b-N_b+g_b\tilde{\gamma}_b)}{D_b+\psi_b}\right]. \tag{65}$$

Similarly we derive the reduced distribution function in the left well around $x=x_0$ using Eq. (35) as (x_0 may be put zero without any loss of generality)

$$\tilde{p}^0_{st}(x_0)=\frac{1}{Z}\sqrt{2\pi D_0}\exp\left[-\frac{\tilde{V}(x_0)+x_0(\Omega_0-N_0+g_0\tilde{\gamma}_0)}{D_0+\psi_0}\right], \tag{66}$$

where we have employed the expansion of $\tilde{V}(x)$ as $\tilde{V}(x)=\tilde{V}(x_0)+(\frac{1}{2})\tilde{\omega}_0^2(x-x_0)^2$ and Z is the normalization constant.

We impose the second boundary condition that at $x=x_0$ the reduced distribution (65) must coincide with Eq. (66) at the bottom of the left well i.e.,

$$\tilde{p}_{st}(x_0)=\tilde{p}^0_{st}(x_0). \tag{67}$$

The above condition is used to determine F_2 in terms of normalization constant Z of Eq. (35)

$$F_2=\frac{1}{Z}\left(\frac{\Lambda}{2\pi}\right)^{1/2}\left(\frac{D_0}{D_b}\right)^{1/2}\times\exp\left[-\frac{\tilde{V}(x_0)+x_0(\Omega_0-N_0+g_0\tilde{\gamma}_0)}{D_0+\psi_0}\right]\times\exp\left[\frac{\tilde{V}(x_b)-\frac{1}{2}\tilde{\omega}_b^2(x_0-x_b)^2+x_0(\Omega_b-N_b+g_b\tilde{\gamma}_b)}{D_b+\psi_b}\right]. \tag{68}$$

Furthermore by explicit evaluation of the normalization constant using the integral

$$\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}p^0_{st}(x,v)dx\,dv=1, \tag{69}$$

where $p^0_{st}(x,v)$ is given by Eq. (35). We obtain

$$Z=\frac{2\pi}{\tilde{\omega}_0}D_0^{1/2}(D_0+\psi_0)^{1/2}\exp\left[\frac{[\Omega_0-N_0+g_0\tilde{\gamma}_0]^2}{2(D_0+\psi_0)\tilde{\omega}_0^2}\right]\times\exp\left[-\frac{\tilde{V}(x_0)+x_0(\Omega_0-N_0+g_0\tilde{\gamma}_0)}{D_0+\psi_0}\right]. \tag{70}$$

Making use of Eq. (70) in Eq. (68) we obtain from Eq. (60) the final expression for quantum Kramers' rate, based on flux-over-population method [2,33], as

$$k=\frac{\tilde{\omega}_0}{2\pi}\left(\frac{\Lambda}{2\pi}\right)^{1/2}\frac{1}{D_b^{1/2}(D_0+\psi_0)^{1/2}}\exp\left(-\frac{[\Omega_0-N_0+g_0\tilde{\gamma}_0]^2}{2(D_0+\psi_0)\tilde{\omega}_0^2}\right)\times\left\{D_b\left(\frac{2\pi D_b}{1+\Lambda D_b}\right)^{1/2}\exp\left(-\frac{\Lambda a^2(\Omega_b-N_b+g_b\tilde{\gamma}_b)^2}{2(1+\Lambda D_b)\tilde{\omega}_b^4}\right)+g_b\left[\left(\frac{\pi}{2\Lambda}\right)^{1/2}\sqrt{2\pi D_b}+I\right]\right\}\times\exp\left(-\frac{E+(\Omega_b-N_b+g_b\tilde{\gamma}_b)(\sqrt{2E}/\tilde{\omega}_b)}{D_b+\psi_b}\right), \tag{71}$$

where we have used the relation (56) to obtain $\tilde{V}(x_0)=\tilde{V}(x_b)-(\frac{1}{2})\tilde{\omega}_b^2(x_0-x_b)^2$ and definition of activation energy as $E=\tilde{V}(x_b)-\tilde{V}(x_0)$.

A close look into the definitions (39a), (40d), and (40e) of Ω, N, and g in the exponential factors in Eq. (71) reveals that each of them is proportional to the anharmonic correction term of the potential, $V'''(x)$ in the leading order so that $[\Omega_0-N_0+g_0\tilde{\gamma}_0]^2/\tilde{\omega}_0^2\sim[V'''(x)]^2/[V''(x)]$, $[\Omega_b-N_b+g_b\tilde{\gamma}_b]^2/\tilde{\omega}_b^4\sim[V'''(x)]^2/[V''(x)]^2$, whereas $[\Omega_b-N_b+g_b\tilde{\gamma}_b]/\tilde{\omega}_b\sim[V'''(x)]/\sqrt{[V''(x)]}$. The last ratio being the dominant contribution the expression (71) then can be simplified as (Ω vanishes in the long time limit)

$$k=\frac{\tilde{\omega}_0}{2\pi}\left(\frac{\Lambda}{2\pi}\right)^{1/2}\frac{1}{D_b^{1/2}(D_0+\psi_0)^{1/2}}\left\{D_b\left(\frac{2\pi D_b}{1+\Lambda D_b}\right)^{1/2}+g_b\left[\left(\frac{\pi}{2\Lambda}\right)^{1/2}\sqrt{2\pi D_b}+I\right]\right\}\times\exp\left(\frac{(N_b-q_b\tilde{\gamma}_b)\sqrt{2E}}{\omega_b(D_b+\psi_b)}\right)\exp\left(-\frac{E}{D_b+\psi_b}\right). \tag{72}$$

The above expression is the quantum Kramers' rate, which is a direct generalization of classical non-Markovian rate valid for intermediate to strong damping regime and for arbitrary decaying correlation function and temperature. The derived rate thus includes the effect of tunneling in a natural way to modify the classical rate.

To recover the classical non-Markovian expression from Eq. (71) one has to take into consideration (i) the system concerned quantum correction due to nonlinearity, i.e., N_b

and g_b must vanish; (ii) the heat bath noise related quantities, e.g., D and ψ are to be calculated from the expressions of the variances (30) using $c(t-t')$ in the classical limit, i.e., Eq. (20). Under these two conditions, Eq. (71) is reduced to the classical expression

$$k=\frac{\tilde{\omega}_0}{2\pi}\left(\frac{\Lambda^c}{1+\Lambda^c D_b^c}\right)^{1/2}\frac{D_b^c}{(D_0^c+\psi_0^c)^{1/2}}\exp\left(-\frac{E}{D_b^c+\psi_b^c}\right), \tag{73}$$

where the superscript "c" signifies the classical limit of the quantum-mechanical quantities, such as $D_0(D_b)$ and $\psi_0(\psi_b)$. The above expression is identical in form to the one derived for classical non-Markovian dynamics [13,14,26].

V. A SPECIFIC EXAMPLE: EXPONENTIALLY CORRELATED MEMORY KERNEL

The structure of $\beta(t)$ given in Eq. (19) suggests that it is quite general and a further calculation requires a prior knowledge of the density of modes $\rho(\omega)$ of the heat bath oscillators. As a specific case we consider in the continuum limit

$$k(\omega)\rho(\omega)=\frac{2}{\pi}\frac{\Gamma}{(1+\omega^2\tau_c^2)} \tag{74}$$

so that $\beta(t)$ takes the well known form of an exponentially correlated memory kernel [34]

$$\beta(t)=\frac{\Gamma}{\tau_c}\exp\left[-\frac{|t|}{\tau_c}\right], \tag{75}$$

where Γ is the damping constant and τ_c refers to the correlation time of the noise. Once we get an explicit expression for $\beta(t)$ and its Laplace transform $\tilde{\beta}(s)=\Gamma/(1+s\tau_c)$, it is possible to make use of Eq. (25) to calculate $\tilde{M}(s)$ and the relaxation function $M(t)$, which for the present case are given by [34]

$$\tilde{M}_0(s)=\frac{s+a_0}{s^3+a_0s^2+b_0+c_0} \tag{76}$$

with

$$a_0=\frac{1}{\tau_c},\quad b_0=\omega_0^2+\frac{\Gamma}{\tau_c},\quad c_0=\frac{\omega_0^2}{\tau_c}$$

and

$$M_0(t)=c_1^0e^{-p_0t}+c_2^0e^{-q_0t}\sin(\epsilon t+\alpha_0), \tag{77}$$

respectively, where

$$p_0=-A_0-B_0+\frac{a_0}{3},\quad q_0=\tfrac{1}{2}(A_0+B_0)+\frac{a_0}{3},$$

$$c=\frac{\sqrt{3}}{2}(A_0-B_0),\quad c_1^0=\frac{1}{2q^0-p^0-d_0},$$

$$d_0=\frac{a_0(2q^0-p^0)-q^{02}-\epsilon^2}{a_0-p^0},$$

$$A_0=\left(\frac{-a_0^3}{27}+\frac{a_0b_0}{6}-\frac{c_0}{2}+\sqrt{R_0}\right)^{1/3},$$

$$B_0=\left(-\frac{a_0^3}{27}+\frac{a_0b_0}{6}-\frac{c_0}{2}-\sqrt{R_0}\right)^{1/3},$$

$$c_2^0=-\frac{c_1^0}{\epsilon}[(d_0-q^0)^2+\epsilon]^{1/2},$$

and

$$\alpha_0=\tan^{-1}\left(\frac{\epsilon}{d_0-q^0}\right) \tag{78}$$

and

$$R_0=-\frac{a_0^2b_0^2}{108}+\frac{b_0^3}{27}+\frac{a_0^3c_0}{27}-\frac{a_0b_0c_0}{6}+\frac{c_0^2}{4}>0$$

for the present problem.

Now making use of the expression (77) for $M(t)$ and expression (18) for correlation function $c(t)$ in Eqs. (30a)–(30c) we calculate explicitly, after a tedious long but straight forward algebra, the time dependent expressions for the variances of the quantum-mechanical mean values of the position and momentum of the particle. These expressions are given by

$$\sigma_{xx}^2(t)=\frac{2h\Gamma}{\pi}\int_0^\infty\frac{\omega}{1+\omega^2\tau_c^2}\left(\coth\frac{\hbar\omega}{2k_bT}\right)\mathcal{F}_x(\omega,t)d\omega$$

$$\sigma_{vv}^2(t)=\frac{2\hbar\Gamma}{\pi}\int_0^\infty\frac{\omega}{1+\omega^2\tau_c^2}\left(\coth\frac{\hbar\omega}{2k_bT}\right)\mathcal{F}_v(\omega,t)d\omega$$

and

$$\sigma_{xv}^2(t)=\tfrac{1}{2}\dot{\sigma}_{xx}^2(t).$$

In Appendix B we provide the explicit structures of $\mathcal{F}_x(\omega,t)$ and $\mathcal{F}_v(\omega,t)$. Since in the long time limit σ_{xv}^2, $\dot{\sigma}_{xv}^2$, $\dot{\sigma}_{vv}^2$ vanish, the calculation of the quantities D_0, D_b, ψ_0, ψ_b essentially rest on the asymptotic values of $\sigma_{xx}^2(t)$ and $\sigma_{vv}^2(t)$ evaluated at the barrier top or the bottom of the well. It must be emphasized that the quantities are nonvanishing at $T=0$ due to quantum fluctuation of the heat bath.

We now turn to the calculation of the relevant asymptotic coefficients g_b and N_b in the expression for the rate (Ω_0 and Ω_b vanish in the long time limit due to the relaxation function). Both of them are related to the convolution integral through the relations (40d) and $g_b=\dot{G}_b$. Since G_b is defined as $\int_0^t M_b(t-\tau)Q_b(\tau)d\tau$, where M_b and Q_b correspond to the barrier top (and M_0 and Q_0 to the bottom of the potential well), we make use of the expressions for M_b and M_0 along with those for Q_b and Q_0 as shown in Appendix A to obtain $G_0(t)$ and $G_b(t)$ and their asymptotic values. Considering

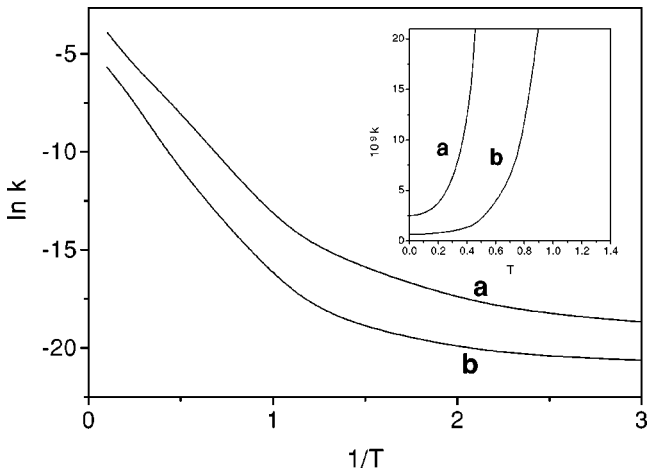

FIG. 1. Plot of ln k vs $1/T$ using Eq. (72) for different values of the damping contant (a) $\Gamma=1.3$, and (b) $\Gamma=1.7$ [Inset: Plot of k vs T illustrate the T^2 dependence at very low temperature. The parameters are same as in the main figure] (units arbitrary).

only the short time linearity of $G_b(t)$ (since the quantum effect in $Q_b(t)$ has been taken into account for the lowest order in the Appendix A) calculation of g_b is quite straight forward. Furthermore the expression for N_b as given by Eq. (40d) can be simplified in the asymptotic limit to obtain

$$N_b(t)=\frac{\dot{M}_b^2 G_b(t)}{M_b^2}.$$

Both g_b and N_b involve the constants $\langle \delta\hat{X}^2\rangle_{t=0}$ and $\langle \delta\hat{X}\,\delta\hat{P}+\delta\hat{P}\,\delta\hat{X}\rangle_{t=0}$, which are assumed to be $\hbar/(2\omega_b)$ (minimum uncertainty state) and zero, respectively, for the present calculation.

To analyze the associated non-Markovian nature of the dynamics at various temperatures it is necessary to go over to numerical simulation of stationary values of D_0, D_b and ψ_0, ψ_b, and Λ. These in turn, are primarily dependent in $\sigma_{xx}^2(t)$ and $\sigma_{vv}^2(t)$, the other variances being vanishing in the long time limit. For the present purpose we assume the simplest form of the cubic potential of the type $V(x)=-(1/3)\bar{A}x^3+\bar{B}x^2$, where the parameter set used is $\bar{A}=0.5$; $\bar{B}=[(3/4)\bar{A}^2E]^{1/3}$; the activation energy $E=V(x_b)-V(x_0)=10$. The correlation time of the noise τ_c is fixed at 0.3. The temperature and the damping constant Γ are varied set to set. The quantities g_b and N_b, which incorporate quantum effects through the anharmonicity of the potential, can be easily calculated numerically as outlined in the previous paragraph. In Fig. 1 we show the Arrhenius plot, i.e., the variation of $\ln k$ vs $1/T$ for two different values of damping constant Γ. It is apparent that in the high temperature regime the plot exhibits linearity, which is the standard Arrhenius classic result. In the low temperature regime, however, one observes a much slower variation that is a typical quantum behavior. To single out this low temperature behavior, we show in the inset of Fig. 1 a clear T^2 dependence of the rate—a feature observed earlier in the recent past [2]. In Figs. 2(a)–(c) we exhibit the variation of the rate k as a function of the damping constant Γ at several temperatures. It is apparent that at a relatively high temperature the rate varies inversely with the damping constant while at low temperature the rate drops at a much faster rate. At $T=0$ the decay is exponential in nature. The quantum rate in this situation essentially corresponds to zero-temperature tunneling. This result is in satisfactory agreement with that of Caldeira and Leggett [20]. The present theory, therefore, unifies the

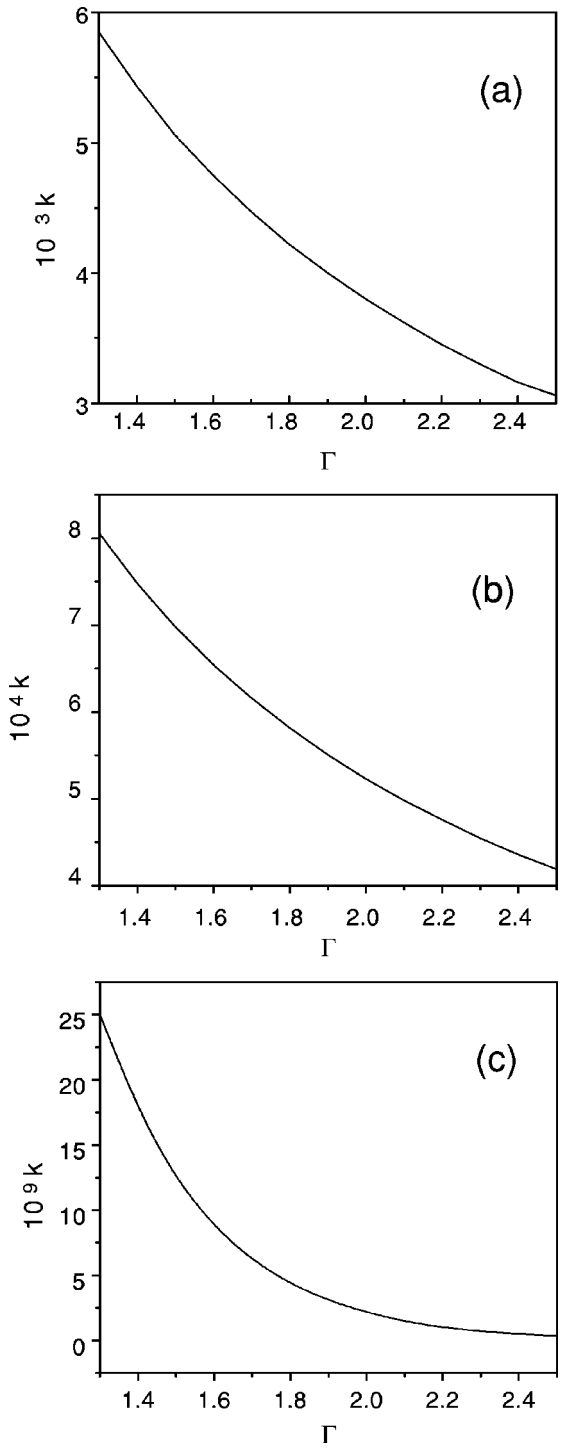

FIG. 2. Plot of quantum Kramers' rate k vs T using Eq. (72) for (a) $T=5.0$, (b) $T=3.0$, and (c) $T=0.0$ (units arbitrary).

aspects of quantum tunneling and thermal noise-induced barrier crossing on the same footing.

VI. CONCLUSIONS

In this paper we have proposed a simple approach to non-Markovian theory of quantum Brownian motion in phase space. Based on an initial coherent state representation of bath oscillators and a canonical equilibrium distribution of quantum-mechanical mean values and their coordinates and momenta, we have shown that it is possible to realize a stochastic differential equation in *c* numbers in the form of a generalized Langevin equation and the associated Fokker-Planck equation that can be recognized as a generalized quantum Kramers' equation. The Kramers' equation is then employed to derive the rate of barrier crossing that includes both tunneling and thermal induced effects on the same footing. The main conclusions in this study are the following.

(i) Our ensemble averaging procedure and the QGLE are amenable to theoretical analysis in terms of the methods developed earlier for the treatment of classical non-Markovian theory of Brownian motion.

(ii) The proposed Kramers' equation is an exact quantum analog of classical generalized Kramers' equation derived earlier in late 1970s by a number of workers. Since we have dealt here with *true probability functions* the theory is free from the problem of singularity or negativity of *quasiclassical* distribution functions, which is often encountered in Wigner equation approaches. The equation is valid for arbitrary temperature and friction.

(iii) The realization of noise as a classical looking entity, which satisfies quantum fluctuation-dissipation relation, allows ourselves to envisage quantum Brownian motion as a quantum generalization of its classical counterpart. The method is based on the canonical quantization procedure and is independent of the path integral formalisms.

(iv) The quantum Kramers' rate [Eq. (71)] is valid for intermediate to strong damping regime and for arbitrary temperature and decaying noise correlations. It reduces to classical non-Markovian rate and purely vacuum fluctuation-induced rate or tunneling in the appropriate limits.

(v) The theory incorporates quantum effects in two different ways. The quantum nature of the system is manifested through the nonlinear part of the potential while the heat bath imparts the usual quantum noise. It must be emphasized that our general analysis takes into consideration the quantum effects of all orders.

(vi) The theory also reveals an interesting interplay of the nonlinearity and dissipation in the Fokker-Planck coefficients that include quantum corrections. The variation of the rate due to tunneling and activation with respect to the temperature and damping has been clearly demonstrated.

The theory presented here is a natural extension of the classical theory of Brownian motion in the sense that the quantum Kramers' equation is *classical-looking in form but quantum-mechanical in its content*. Also we have considered only the spatial diffusion-limited regime in the calculation of the rate. It is worthwhile to extend the approach to the energy diffusion regime and further to implement other methods of the treatment of classical Brownian motion.

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APPENDIX A: CALCULATION OF QUANTUM DISPERSION *Q*

The quantum fluctuation Q is defined in Eq. (15) as

$$Q(t)=V'(\langle\hat{X}\rangle)-\langle V'(\hat{X})\rangle. \tag{A1}$$

So far as the general formulation of the theory upto Sec IV is concerned Q is taken in full. Or in other words the quantum Kramers' equation (32) or the rate Eq. (71) incorporates quantum effects due to the system in all orders. However, in actual calculations Q has to be estimated order by order [35]. To this end we consider the lowest order quantum corrections. Returning to the quantum mechanics of the system in Heisenberg picture, it is convenient to write the operators $\hat{X}$ and $\hat{P}$ as

$$\hat{X}(t)=\langle\hat{X}(t)\rangle+\delta\hat{X},$$

$$\hat{P}(t)=\langle\hat{P}(t)\rangle+\delta\hat{P}, \tag{A2}$$

where $\langle\hat{X}(t)\rangle$ and $\langle\hat{P}(t)\rangle$ are the quantities signifying quantum-mechanical averages and $\delta\hat{X}$ and $\delta\hat{P}$ are quantum corrections. By construction $\langle\delta\hat{X}\rangle$ and $\langle\delta\hat{P}\rangle$ are zero and $\delta\hat{X}$ and $\delta\hat{P}$ obey the commutation relation $[\delta\hat{X},\delta\hat{P}]=ih$. Using Eq. (A2) in $\langle V'(\hat{X})\rangle$ and a Taylor expansion around $\langle\hat{X}\rangle$ it is possible to express $Q(t)$ as (keeping the lowest order nonvanishing term)

$$Q(t)=-\frac{1}{2}V'''(\langle\hat{X}\rangle)\langle\delta\hat{X}^2(t)\rangle \tag{A3}$$

where $\langle\hat{X}\rangle$ and $\langle\delta\hat{X}^2\rangle$ follow a coupled set of equations as given below

$$\langle\dot{\hat{X}}\rangle=\langle\hat{P}\rangle,$$

$$\langle\dot{\hat{P}}\rangle=-V'(\langle\hat{X}\rangle),$$

$$\frac{d}{dt}\langle\delta\hat{X}^2\rangle=\langle\delta\hat{X}\,\delta\hat{P}+\delta\hat{P}\,\delta\hat{X}\rangle,$$

$$\frac{d}{dt}\langle\delta\hat{X}\,\delta\hat{P}+\delta\hat{P}\,\delta\hat{X}\rangle=2\langle\delta\hat{P}^2\rangle-V''(\langle\hat{X}\rangle)\langle\delta\hat{X}^2\rangle$$

$$\frac{d}{dt}\langle\delta\hat{P}^2\rangle=-V''(\langle\hat{X}\rangle)(\langle\delta\hat{X}\,\delta\hat{P}+\delta\hat{P}\,\delta\hat{X}\rangle \tag{A4}$$

The above set of equations can be derived from Heisenberg's equation of motion. In the Kramers' problem one is

primarily concerned with the local dynamics of the system around the barrier top at $\langle\hat{X}\rangle(=x)=x_b$ or at the bottom at $\langle\hat{X}\rangle(=x)=x_0$. The solution depends critically on the nature of the curvature of the potential, i.e., $V''(\langle X\rangle)$. Considering the local nature of the dynamics we have expressed $V''(x=x_b)=-\omega_b^2$ and $V''(x=x_0)=\omega_0^2$ and consequently the equations for the quantum corrections can be solved independently of the first two of Eqs. (A4). A solution of $\langle\delta\hat{X}^2\rangle$ around $x=x_0$, which is an elliptic fixed point is therefore given by

$$\langle\delta\hat{X}^2(t)\rangle_{x\sim x_0}=\tfrac{1}{2}\left[\langle\delta\hat{X}^2\rangle_{t=0}-\frac{\langle\delta\hat{P}^2\rangle_{t=0}}{\omega_0^2}\right]\cos(2\omega_0 t)+\frac{\langle\delta\hat{X}\,\delta\hat{P}+\delta\hat{P}\,\delta X\rangle_{t=0}}{2\omega_0}\sin(2\omega_0 t)+\frac{2I_0^c}{4\omega_0^2}, \tag{A5}$$

where I_0^c is an integration constant and is given by $I_0^c=\langle\delta\hat{P}^2\rangle_{t=0}+\omega_0^2\langle\delta X^2\rangle_{t=0}$. Therefore, the quantum dispersion at the bottom of the well is given by

$$Q_0(t)=-\tfrac{1}{2}V'''(x_0)\langle\delta\hat{X}^2(t)\rangle_{x\sim x_0}, \tag{A6}$$

where $\langle\delta\hat{X}^2(t)\rangle_{x\sim x_0}$ is governed by Eq. (A5). Similarly we calculate quantum fluctuation $Q_b(t)$ near the top of the potential barrier at $x=x_b$ as

$$Q_b(t)=-\tfrac{1}{2}V'''(x_b)\langle\delta\hat{X}^2(t)\rangle_{x\sim x_b}, \tag{A7}$$

where $\langle\delta\hat{X}^2(t)\rangle_{x\sim x_b}$ in a solution of the last three equations of Eqs. (A4) around $x\sim x_b$ and is given by

$$\langle\delta\hat{X}^2(t)\rangle_{x\sim x_b}=\langle\delta\hat{X}^2\rangle_{t=0}\cosh(2\omega_b t)+\frac{\langle\delta\hat{X}\,\delta\hat{P}+\delta\hat{P}\,\delta\hat{X}\rangle_{t=0}}{2\omega_b}\sinh(2\omega_b t) \tag{A8}$$

It is interesting to note the hyperbolic nature of the top of the barrier that is reflected in the exponential divergence of the quantum fluctuations. This point has been studied extensively in the recent literature in the context of chaos [36–39]. Having evaluated the quantum dispersions $Q_0(t)$ and $Q_b(t)$, we are now in a position to calculate several related quantities such as $G(t)$, $N(t)$, $\Omega(t)$, and $g(t)$. A better estimate of the quantum correction Q can be obtained from the solutions of the equations of higher order corrections derived earlier by Sundaram and Milonni [35].

APPENDIX B: CALCULATION OF $\mathcal{F}_x(\omega,T)$ AND $\mathcal{F}_V(\omega,T)$

The expressions $\mathcal{F}_x(\omega,t)$ and $\mathcal{F}_v(\omega,t)$ are given by

$$\mathcal{F}_x(\omega,t)=\int_0^t M_0(t_1)[c_1^0 I_1(t_1)+c_2^0 I_2(t_1)]dt_1 \tag{B1}$$

and

$$\mathcal{F}_v(\omega,t)=\int_0^t N_0(t_1)[p^0 c_1^0 I_1(t_1)+q_0 c_2^0 I_2(t_1)-c_2^0\epsilon I_3(t_1)]dt_1, \tag{B2}$$

where

$$N_0(t)=c_1^0 p^0 e^{-p^0 t}+c_2^0 q^0 e^{-q^0 t}\sin(\epsilon t+\alpha)-c_2^0\epsilon e^{-q^0 t}\times\cos(\epsilon t+\alpha). \tag{B3}$$

Here I_1, I_2, and I_3 are given by the following expressions.

$$I_1=-B_{2j}e^{-pt_1}+B_{2j}\cos\omega_j t_1+B_{1j}\sin\omega_j t_1, \tag{B4}$$

$$\begin{aligned}I_2=\tfrac{1}{2}[&-B_{4j}\cos(\omega_j t_1+\alpha)+B_{4j}e^{-qt_1}\cos(\omega_j t_1+\alpha)\\&\times\cos(\omega_{j-}t_1)+B_{6j}e^{-qt_1}\cos(\omega_j t_1+\alpha)\times\sin(\omega_{j-}t_1)\\&\pm B_{6j}\sin(\omega_j t_1+\alpha)-B_{6j}e^{-qt_1}\sin(\omega_j t_1+\alpha)\\&\times\cos(\omega_{j-}t_1)+B_{4j}e^{-qt_1}\times\sin(\omega_j t_1+\alpha)\sin(\omega_{j-}t_1)\\&+B_{3j}\cos(\omega_j t_1-\alpha)-B_{3j}e^{-qt_1}\cos(\omega_j t_1-\alpha)\\&\times\cos(\omega_{j+}t_1)-B_{5j}e^{-qt_1}\cos(\omega_j t_1-\alpha)\sin(\omega_{j+}t_1)\\&+B_{5j}\sin(\omega_j t_1-\alpha)-B_{5j}e^{-qt_1}\sin(\omega_j t_1-\alpha)\\&\times\cos(\omega_{j+}t_1)+B_{3j}e^{-qt_1}\sin(\omega_j t_1-\alpha)\sin(\omega_{j+}t_1)],\end{aligned} \tag{B5}$$

$$\begin{aligned}I_3=\tfrac{1}{2}[&B_{6j}\cos(\omega_j t_1+\alpha)-B_{6j}e^{-qt_1}\cos(\omega_j t_1+\alpha)\\&\times\cos(\omega_{j-}t_1)+B_{4j}e^{-qt_1}\cos(\omega_j t_1+\alpha)\\&\times\sin\omega_{j-}t_1+B_{4j}\sin(\omega_j t_1+\alpha)\\&-B_{4j}e^{-qt_1}\sin(\omega_j t_1+\alpha)\cos(\omega_{j-}t_1)-B_{6j}e^{-qt_1}\\&\times\sin(\omega_j t_1+\alpha)\sin(\omega_{j-}t_1)+B_{5j}\\&\times\cos(\omega_j t_1-\alpha)-B_{5j}e^{-qt_1}\cos(\omega_j t_1-\alpha)\times\cos(\omega_{j+}t_1)\\&+B_{3j}e^{-qt_1}\cos(\omega_j t_1-\alpha)\sin(\omega_{j+}t_1)+B_{3j}\sin(\omega_j t_1-\alpha)\\&-B_{3j}e^{-qt_1}\times\sin(\omega_j t_1-\alpha)\cos(\omega_{j+}t_1)\\&-B_{5j}e^{-qt_1}\sin(\omega_j t_1-\alpha)\sin(\omega_{j+}t_1)],\end{aligned} \tag{B6}$$

where

$$\omega_{j+}=\omega_j+\alpha,\quad \omega_{j-}=\omega_j-\alpha,$$

$$B_{1j}=\frac{\omega_j}{p^2+\omega_j^2},\quad B_{2j}=\frac{p}{p^2+\omega_j^2},$$

$$B_{3j}=\frac{\omega_{j+}}{q^2+\omega_{j+}{}^2},\quad B_{4j}=\frac{\omega_{j-}}{q^2+\omega_{j-}{}^2},$$

$$B_{5j}=\frac{q}{q^2+\omega_{j+}{}^2},\quad B_{6j}=\frac{q}{q^2+\omega_{j-}{}^2}.$$

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