Quantum Kramers turnover: a phase space function approach

Debashis Barik and Deb Shankar Ray∗

Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India

The problem of Kramers’ turnover is a central issue of dynamical theory of reaction rate. Since its classical solution in the Markovian limit in mid-eighties by Melnikov and Meshkov, the problem has been addressed by a number of groups in the last decade both in classical non-Markovian and quantum mechanical context. Based on a coherent state representation of noise operators and a positive definite Wigner canonical thermal distribution function we have recently developed a c-number quantum Langevin equation [Barik et al, J. Chem. Phys. 119, 680 (2003); Banerjee et al, Phys. Rev. E 65, 021109 (2002)]. We implement this scheme within Pollak’s well known normal mode description to calculate the quantum transmission coefficient over an arbitrary range of friction, noise correlation and temperature. The theory generalizes the quantum correction to Grote-Hynes factor in the rate expression down to vacuum limit which reduces to well known high temperature quantum correction, i.e., the Wolynes term for quantum transmission and reflection for the barrier in the appropriate limit and also considers the quantum corrections due to nonlinearity of the system potential order by order which contributes to energy loss and dispersion due to coupling between unstable and stable normal modes near the barrier top and is valid for both above and below the activated tunneling regime. Our results have been compared with those obtained earlier for a model potential and found to be good agreement.

I. INTRODUCTION

Kramers’ diffusion model of chemical reactions proposed in 1940 forms the dynamical basis of modern rate theory of activated processes. The seminal and essential content of this nonequilibrium formulation is the inclusion of dependence of rate constant of a reaction on viscosity or friction of the reaction medium. Based on the classical theory of Brownian motion in phase space Kramers derived the expressions for nonequilibrium steady state distribution functions to work out the rate coefficients in the two different limiting situations and showed that the rate varies linearly in the weak dissipation regime and inversely in the high dissipation regime with friction. That is, in between the energy diffusion and spatial diffusion limited regimes the rate constant as a function of friction exhibits a bell-shaped curve - known as Kramers’ turnover. With the advent of ultrafast lasers and time-resolved detection techniques since late seventies, experimental confirmation of Kramers’ theory provided a new impetus for further development in chemical dynamics and condensed matter physics [2, 3, 4, 5, 6].

In spite of this spectacular growth one point however, that remained illusive for several decades was the absence of an analytic rate formulae which correctly interpolates the two limits. A significant advancement was made in 1986 when Melnikov and Meshkov [7, 8] proposed a theory of Kramers turnover for Markovian friction. The key point of this analysis is the calculation of an average energy loss of the system due to its weak coupling with the bath modes near the top of the potential barrier. The approach was further extended to non-Markovian domain by Pollak, Grabert and Hänggi [9] within the framework of a normal mode description of the system plus reservoir, where the implementation of an ad hoc function in the expression for the spatial diffusion limited rate could be avoided. Subsequent to this formulation of classical theory, the problem of quantum Kramers’ turnover was addressed by Rips and Pollak [10]. The degree of accuracy of classical and quantum theories has been tested by numerical simulation of reaction rate with model potentials. We refer to Refs.11-16 for further details.

The classical theory of Kramers’ turnover uses a Langevin description that governs the dynamics of the system by an infinite number of harmonic oscillators coupled linearly to the system degree of freedom. Very recently based on a coherent state representation of noise operator and a positive definite Wigner canonical thermal distribution of harmonic oscillators [17] of the bath we have proposed a c-number quantum Langevin equation [18, 19, 20, 21, 22, 23] in the context of quantum rate theory and stochastic processes in terms of phase space function formalism [24, 25]. It would seem that one should be able to analyze a quantum turnover for arbitrary noise correlation and temperature by using such a c-number formulation. This is the main purpose of this paper. In what follows we make use of a c-number Hamiltonian in the normal mode procedure and take care of the nonequilibrium dynamics at the barrier top by calculating the average quantum energy loss of the unstable mode due to its weak coupling with the stable bath modes and equilibration in the well by a Wigner thermal distribution. Besides being an approach based on canonical quantization the theory specifically addresses the following three points: First, we quantize the system

∗ Email Address: pcdsr@mahendra.iacs.res.in
mode to make the theory applicable beyond the activated tunneling regime down to absolute zero. Second, although harmonic approximation is a good description at the barrier top, actual shape and nonlinearity of the system potential is important at low temperatures; but systematic corrections to harmonic approximation have hardly been envisaged. The present formulation takes care of quantum corrections due to nonlinearity of the system degrees of freedom by order. Again even in the lowest order this quantum correction can be, in principle, a contribution in the weak coupling between the stable and unstable modes for calculation of energy loss and dispersion as shown in this paper. Third, we take into account of the quantum correction to Grote-Hynes dynamical factor in the rate expression down to vacuum limit. This reduces to well-known high temperature quantum correction or the Wolynes [26] term in the appropriate limit. The approach thus generalizes the Wolynes term in the deep tunneling regime.

The outlay of the paper is as follows. In the following section II we discuss our c-number quantum Langevin equation which allows us to realize a c-number Hamiltonian analyzed by Pollak’s normal mode analysis. The equilibrium theory in terms of Wigner distribution function to formulate a quantum counterpart of multidimensional transition state theory (TST) has been presented in Sec.III. Sec.IV is devoted to nonequilibrium dynamics of the unstable mode and its average energy loss over round trip time in the well near the barrier top. Since this energy is sensitive to quantum contribution due to nonlinearity of the potential we calculate the quantum correction to energy loss of the unstable mode explicitly in Sec.V. An explicit example with cubic potential has been worked out in Sec.VI to compare with the known results. The paper is concluded in Sec.VII.

II. C-NUMBER QUANTUM LANGEVIN EQUATION

We consider a particle of unit mass coupled to a medium comprised of a set of harmonic oscillators with frequency $\omega_i$. This is described by the following Hamiltonian:

$$H = \frac{\hat{p}^2}{2} + V(\hat{q}) + \sum_{i=1}^{N} \left\{ \frac{\hat{p}_i^2}{2} + \frac{1}{2}(\omega_i \hat{x}_i - \frac{c_i}{\omega_i} \hat{q})^2 \right\}$$

(2.1)

Here $\hat{q}$ and $\hat{p}$ are co-ordinate and momentum operators of the particle and the set $\{\hat{x}_i, \hat{p}_i\}$ is the set of co-ordinate and momentum operators for the reservoir oscillators coupled linearly to the system through their coupling coefficients $c_i$. The potential $V(\hat{q})$ is due to the external force field for the Brownian particle. The co-ordinate and momentum operators follow the usual commutation relations $[\hat{q}, \hat{p}] = i\hbar$ and $[\hat{x}_i, \hat{p}_j] = i\hbar \delta_{ij}$.

Eliminating the reservoir degrees of freedom in the usual way we obtain the operator Langevin equation for the particle,

$$\ddot{\hat{q}}(t) + \int_{0}^{t} dt' \gamma(t - t') \dot{\hat{q}}(t') + V'(\hat{q}) = \hat{F}(t) ,$$

(2.2)

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

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

(2.3)

and

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

(2.4)

Here masses have been assumed to be unity.

The Eq. (2.2) is the well known exact quantized operator Langevin equation for which the noise properties of $\hat{F}(t)$ can be derived by using a suitable initial canonical distribution of the bath co-ordinate and momentum operators at $t = 0$ as follows;
\[ \langle \hat{F}(t) \rangle_{QS} = 0 \] 
(2.5)
\[ \frac{1}{2} \left\{ \langle \hat{F}(t) \rangle_{\mathcal{O}} + \langle \hat{F}(t') \hat{F}(t) \rangle_{QS} \right\} \]
(2.6)
\[ = \frac{1}{2} \sum_{j=1}^{N} \frac{c_j^2}{\omega_j^2} \hbar \omega_j \left( \coth \frac{\hbar \omega_j}{2 k_B T} \right) \cos \omega_j (t - t') \]
(2.7)

where \( \langle \ldots \rangle_{QS} \) refers to quantum statistical average on bath degrees of freedom and is defined as
\[ \langle \hat{O} \rangle_{QS} = \frac{\text{Tr} \hat{O} \exp(-\hat{H}_{\text{bath}}/k_B T)}{\text{Tr} \exp(-\hat{H}_{\text{bath}}/k_B T)} \]
(2.8)

for any operator \( \hat{O}(\{\omega_j^2/c_j\hat{x}_j - \hat{q}_j\},\{\hat{p}_j\}) \) where \( \hat{H}_{\text{bath}}(\sum_{j=1}^{N} (\hat{p}_j^2/2 + 1/2(\omega_j \hat{x}_j - \hat{q}_j)^2)) \) at \( t = 0 \). By Trace we mean the usual quantum statistical average. Eq. (2.7) is the fluctuation-dissipation relation with the noise operators ordered appropriately in the quantum mechanical sense.

To construct a c-number Langevin equation we proceed from Eq. (2.2). We first carry out the quantum mechanical average of Eq. (2.2)

\[ \langle \hat{q}(t) \rangle + \int_{0}^{t} dt' \gamma(t - t') \langle \hat{q}(t') \rangle + \langle V'(\hat{q}) \rangle = \langle \hat{F}(t) \rangle \]
(2.9)

where the quantum mechanical average \( \langle \ldots \rangle \) is taken over the initial product separable quantum states of the particle and bath oscillators at \( t = 0 \), \( |\phi \rangle \{ |\alpha_1 \rangle |\alpha_2 \rangle \ldots |\alpha_N \rangle \} \). Here \( |\phi \rangle \) denotes any arbitrary initial state of the particle and \( |\alpha_j \rangle \) corresponds to the initial coherent state of the \( j \)-th bath oscillator. \( |\alpha_j \rangle \) is given by \( |\alpha_j \rangle = \exp(\langle |\omega_j|/c_j \rangle^2) \sum_{n_j=0}^{\infty} (\alpha_j^{n_j}/\sqrt{n_j!}) |n_j \rangle \), \( \omega_j \) being expressed in terms of the mean values of the shifted co-ordinate and momentum of the \( j \)-th oscillator, \( \{ (\omega_j^2/c_j)(\hat{x}_j(0) - \langle \hat{q}(0) \rangle) \} = (\sqrt{\hbar/2\omega_j}(\alpha_j + \alpha_j^*) \) and \( \langle \hat{p}_j(0) \rangle = i\sqrt{\hbar/2}(\alpha_j^* - \alpha_j) \), respectively. It is important to note that \( \langle \hat{F}(t) \rangle \) of Eq. (2.4) is a classical-like noise term which, in general, is a non-zero number because of the quantum mechanical averaging and is given by \( \langle \langle \hat{F}(t) \rangle \equiv f(t) \);

\[ f(t) = \sum_{j} \left[ \frac{\omega_j^2}{c_j} \langle \hat{x}_j(0) - \langle \hat{q}(0) \rangle \rangle \right] \frac{c_j^2}{\omega_j^2} \cos \omega_j t + \frac{c_j}{\omega_j} \langle \hat{p}_j(0) \rangle \sin \omega_j t \]
(2.10)

It is convenient to rewrite the c-number equation (2.10) as follows;

\[ \langle \ddot{\hat{q}}(t) \rangle + \int_{0}^{t} dt' \gamma(t - t') \langle \dot{\hat{q}}(t') \rangle + \langle V'(\hat{q}) \rangle = f(t) \]
(2.11)

To realize \( f(t) \) as an effective c-number noise we now introduce the ansatz that the momenta \( \langle \hat{p}_j(0) \rangle \) and the shifted co-ordinates \( \{ (\omega_j^2/c_j)(\hat{x}_j(0) - \langle \hat{q}(0) \rangle) \} \), \( \{ \hat{p}_j \} \) of the bath oscillators are distributed according to a canonical distribution of Gaussian form as

\[ P_j = N \exp \left\{ -\frac{[\langle \hat{p}_j(0) \rangle^2 + \frac{c_j^2}{\omega_j^2} (\langle \hat{x}_j(0) \rangle - \langle \hat{q}(0) \rangle)^2]}{2\hbar \omega_j (n_j(\omega_j) + \frac{1}{2})} \right\} \]
(2.12)

so that for any function of the quantum mechanical mean values \( O_j \{ \langle \hat{p}_j(0) \rangle, (\omega_j^2/c_j)(\langle \hat{x}_j(0) \rangle - \langle \hat{q}(0) \rangle) \} \) the statistical average \( \langle \ldots \rangle_S \) is

\[ \langle O_j \rangle_S = \int O_j \ P_j \ d\langle \hat{p}_j(0) \rangle \ d\{ (\omega_j^2/c_j)(\langle \hat{x}_j(0) \rangle - \langle \hat{q}(0) \rangle) \} \]
(2.13)
Here $\bar{n}_j$ indicates the average thermal photon number of the $j$-th oscillator at temperature $T$ and $\bar{n}_j(\omega_j) = 1/\exp(\hbar \omega_j/k_B T) - 1$ and $N$ is the normalization constant.

The distribution (2.14) and the definition of statistical average (2.15) imply that $f(t)$ must satisfy

$$\langle f(t) \rangle_S = 0 \quad (2.14)$$

and

$$\langle f(t) f(t') \rangle_S = \frac{1}{2} \sum_j c_j^2 \hbar \omega_j \left( \coth \frac{\hbar \omega_j}{2 k_B T} \right) \cos \omega_j (t - t') \quad (2.15)$$

That is, $c$-number noise $f(t)$ is such that it is zero-centered and satisfies the standard fluctuation-dissipation relation (FDR) as expressed in Eq.(2.17). It is important to emphasize that the ansatz (2.12) is a canonical Wigner distribution for a shifted harmonic oscillator (17) which remains always a positive definite function. A special advantage of using this distribution is that it remains valid as pure state non-singular distribution function at $T = 0$. Furthermore, this procedure allows us to bypass the operator ordering prescription of Eq.(2.17) for deriving the noise properties of the bath in terms of fluctuation-dissipation relation and to identify $f(t)$ as a classical looking noise with quantum mechanical content.

We now return to Eq.(2.11) to add the force term $V'(\langle \hat{q} \rangle)$ on both sides of Eq.(2.11) and rearrange it to obtain

$$\dot{\hat{q}} = p \quad (2.16)$$

$$\dot{\hat{p}} = -\int_0^t dt' \gamma(t - t') p(t') - V'(q) + f(t) + Q(t) \quad (2.17)$$

where we put $\langle \hat{q}(t) \rangle = q(t)$ and $\langle \hat{p}(t) \rangle = p(t)$ for notational convenience and

$$Q(t) = V'(\langle \hat{q} \rangle) - \langle V'(\hat{q}) \rangle \quad (2.18)$$

represents the quantum correction due to the system degrees of freedom. Eq.(2.17) offers a simple interpretation. This implies that the quantum Langevin equation is governed by a $c$-number quantum noise $f(t)$ originating from the heat bath characterized by the properties (2.14) and (2.15) and a quantum fluctuation term $Q(t)$ (18, 19, 20, 21, 22, 23) characteristic of the non-linearity of the potential (24).

Referring to the quantum nature of the system in the Heisenberg picture, one may writes.

$$\dot{\hat{q}}(t) = q + \delta \hat{q} \quad (2.19)$$

$$\dot{\hat{p}}(t) = p + \delta \hat{p} \quad (2.20)$$

where $\langle \hat{q} \rangle (= q)$ and $\langle \hat{p} \rangle (= p)$ are the quantum-mechanical averages and $\delta \hat{q}$, $\delta \hat{p}$ are the operators. By construction $\langle \delta \hat{q} \rangle$ and $\langle \delta \hat{p} \rangle$ are zero and $\langle [\delta \hat{q}, \delta \hat{p}] \rangle = i \hbar$. Using Eqs.(2.19) and (2.20) in $\langle V'(\hat{q}) \rangle$ and a Taylor series expansion around $\langle \hat{q} \rangle$ it is possible to express $Q(t)$ as

$$Q(t) = -\sum_{n \geq 2} \frac{1}{n!} V^{(n+1)}(q) \langle \delta \hat{q}^n(t) \rangle \quad (2.21)$$

Here $V^{(n)}(q)$ is the $n$-th derivative of the potential $V(q)$. For example, the second order $Q(t)$ is given by $Q(t) = -\frac{1}{2} V''(q) \langle \delta \hat{q}^2(t) \rangle$. The calculation of $Q(t)$ (18, 19, 20, 21, 22, 23, 27, 28) therefore rests on quantum correction terms, $\langle \delta \hat{q}^n(t) \rangle$ which are determined by solving the quantum correction equations as discussed in the Sec.V.

The e-number Hamiltonian corresponding to Langevin equation (2.16, 2.17) is given by

$$H = \frac{p^2}{2} + \left[ V(q) + \sum_{n \geq 2} \frac{1}{n!} V^{(n)}(q) \langle \delta \hat{q}^n \rangle \right] + \sum_{i=1}^N \left\{ \frac{p_i^2}{2} + \frac{1}{2} (\omega_i x_i - c_i \hat{q})^2 \right\} \quad (2.22)$$
Note that the above Hamiltonian is different from our starting Hamiltonian operator (2.1) because of the c-number nature of (2.22). \( \{ x_i, p_i \} \) are the quantum mean value of the co-ordinate and the momentum operators of the bath oscillators.

The spectral density function is defined as

\[
J(\omega) = \frac{\pi}{2} \sum_{i=1}^{N} \frac{c_i^2}{\omega_i} \delta(\omega - \omega_i) \tag{2.23}
\]

We now assume that at \( q = 0 \), the potential \( V(q) \) has a barrier with height \( V^\dagger \) such that a harmonic approximation around \( q = 0 \) leads to

\[
V(q) = V^\dagger - \frac{1}{2} \omega_b^2 q^2 + V_2(q) \tag{2.24}
\]

where \( \omega_b^2 = V''(q) \mid_{q=0} \), refers to the second derivative of the potential \( V(q) \). \( \omega_b \) is the frequency at the barrier top and \( V_2(q) \) is the non-linear part of the classical potential and is given by \( V_2 = \sum_{n \geq 3} \frac{1}{n!} \frac{\partial^n V(q)}{\partial q^n} \mid_{q=0} q^n \). With Eq. (2.24) the quantum correction part in the Hamiltonian Eq. (2.22) becomes

\[
\sum_{n \geq 2} \frac{1}{n!} V^{(n)}(q) \langle \delta q^n \rangle = -\frac{\omega_b^2}{2} B_2 + V_3(q) \tag{2.25}
\]

where \( B_n = \langle \delta q^n \rangle; V_3 = \sum_{n \geq 2} \frac{B_n}{n!} \frac{\partial^n V_2(q)}{\partial q^n} \). Note that we have introduced an approximation by putting a bar over quantum dispersion \( \langle \delta q^n(t) \rangle \) to indicate its time average since we will be concerned here with the energy loss of the system mode averaged over one round trip time, i.e., the time required to traverse from one turning point of the potential well to another and back. We will discuss this averaging in greater detail in Sec.V. Putting (2.24) and (2.25) in the Hamiltonian (2.22) we obtain

\[
H = H_0 + V_N(q) \tag{2.26}
\]

where we have decomposed the Hamiltonian in the harmonic part \( H_0 \) and the anharmonic part \( V_N(q) \) as

\[
H_0 = \left[ \frac{p^2}{2} + \sum_i \frac{p_i^2}{2} \right] + \left[ V_1^\dagger - \frac{1}{2} \omega_b^2 q^2 + \sum_i \frac{1}{2} \left( \omega_i x_i - c_i \omega_i q \right)^2 \right] \tag{2.27}
\]

and

\[
V_N(q) = V_2(q) + V_3(q) \tag{2.28}
\]

\[
and \quad V_1^\dagger = V^\dagger - \frac{B_2}{2} \omega_b^2
\]

\( V_2(q) \) and \( V_3(q) \) are therefore classical and quantum anharmonic contributions to total anharmonic part of the Hamiltonian. The separability of the c-number Hamiltonian in the quadratic and nonlinear parts allows us to make a normal mode transformation to convert the quadratic Hamiltonian into a diagonal form. The method of normal mode analysis has been used extensively by Pollak and co-workers in classical and quantum theories of activation, tunneling and dephasing. For details we refer to [Ref. 9,10,27-30].

Following Pollak, we diagonalize the force constant matrix \( T \) of the Hamiltonian (2.24) with the matrix \( U \)

\[
UT = \lambda^2 U \tag{2.29}
\]

where \( U \) provides the transformation from old co-ordinates to the normal co-ordinates.
\[
\begin{pmatrix}
\rho \\
y_1 \\
y_2 \\
\vdots \\
y_N
\end{pmatrix}
= U
\begin{pmatrix}
x_1 \\
x_2 \\
\vdots \\
x_N
\end{pmatrix}
\] (2.30)

The c-number Hamiltonian of the unstable normal co-ordinate is given by

\[
H_0 = \frac{1}{2} \dot{\rho}^2 + V_1^{\downarrow} - \frac{1}{2} \lambda_b^2 \rho^2 + \sum_{i=1}^{N} \left( \frac{1}{2} \left( y_i^2 + \lambda_i^2 y_i^2 \right) \right)
\] (2.31)

The eigenvalues \(\lambda_i^2\) and \(\lambda_b^2\) are expressible in terms of the coupling constant of the system and the bath implicitly as follows:

\[
\lambda_b^2 = \omega_b^2 \left[ 1 + \sum_{j=1}^{N} \frac{c_j^2}{\omega_j^2 (\omega_j^2 + \lambda_b^2)} \right] \] (2.32)

\[
\lambda_i^2 = -\omega_i^2 \left[ 1 + \sum_{j=1}^{N} \frac{c_j^2}{\omega_j^2 (\omega_j^2 - \lambda_i^2)} \right], \quad i = 1, 2, \ldots N
\] (2.33)

where (2.32) and (2.33) correspond to normal mode frequencies of the unstable mode and the i-th bath oscillator respectively.

The transformation (2.30) implies

\[
q = u_{00} \rho + \sum_{j=1}^{N} u_{j0} y_j
\] (2.34)

and it has been shown \[9\] that \(u_{00}\) and \(u_{j0}\) may be expressed as

\[
u_{00}^2 = \left[ 1 + \sum_{j=1}^{N} \frac{c_j^2}{(\omega_j^2 + \lambda_b^2)^2} \right]^{-1}
\] (2.35)

and

\[
u_{j0}^2 = \left[ 1 + \sum_{j=1}^{N} \frac{c_j^2}{(\lambda_j^2 - \omega_j^2)^2} \right]^{-1}
\] (2.36)

Making use of the spectral density function (2.23) and Laplace transformation of \(\gamma(t)\) Eq. (2.32) and Eq. (2.35) may be written in the continuum limit as

\[
\lambda_b^2 = \frac{\omega_b^2}{1 + \gamma(\lambda_b)/\lambda_b}
\] (2.37)

and

\[
u_{00}^2 = \left[ 1 + \frac{2}{\pi} \int_0^\infty d\omega J(\omega) \frac{\omega}{(\lambda_b^2 + \omega^2)^2} \right]^{-1}
\] (2.38)
The two important identities in relation to orthogonal transformation matrices and the associated frequencies may be noted here for the dynamics at the barrier top and at the bottom of the well:

\[ \omega^2_b \prod_{i=1}^{N} \omega_i^2 = \lambda^2_b \prod_{i=1}^{N} \lambda_i^2 \]  

(2.39)

and

\[ \omega^2_0 \prod_{i=1}^{N} \omega_i^2 = \lambda^2_0 \prod_{i=1}^{N} \Lambda_i^2 \]  

(2.40)

Here \( \omega_0 \) and \( \lambda_0 \) are the frequencies of the system at the bottom of the well in the original co-ordinate and normal co-ordinate respectively. Similarly \( \Lambda_i \) corresponds to the normal mode frequencies of the bath oscillators corresponding to a normal mode Hamiltonian at the bottom of the well,

\[ H'_0 = \frac{1}{2} \dot{\rho'}^2 + \frac{1}{2} \lambda^2_0 \rho'^2 + \left\{ \sum_{i=1}^{N} \frac{1}{2} y_i'^2 + \frac{1}{2} \Lambda_i^2 y_i'^2 \right\} \]  

(2.41)

Here \( \rho' \) and \( \dot{\rho'} \) are coordinate and momentum of system mode respectively and \( y_i' \) and \( \dot{y}_i' \) are coordinate and momentum of \( i \)th bath oscillator respectively at the bottom of the well in the normal coordinates. \( \lambda_0 \) and \( \Lambda_i \) are given by

\[ \lambda^2_0 = \frac{\omega^2_0}{1 + \sum_{j=1}^{N} \frac{c_j^2}{\omega_j^2 (\omega_j^2 - \lambda^2_0)}} \]  

(2.42)

\[ \Lambda_i^2 = \frac{\omega^2_0}{1 + \sum_{j=1}^{N} \frac{c_j^2}{\omega_j^2 (\omega_j^2 - \Lambda_j^2)}} , \quad i = 1, 2...N \]  

(2.43)

The description of a Kramers’ turnover of the rate constant from low to high friction limit requires the coupling between the normal modes. An important parameter which is relevant for describing the coupling perturbatively has been defined by

\[ \epsilon = \left( \frac{1}{u_{00}^2} - 1 \right) = \sum_{j=1}^{N} \left( \frac{u_{j0}}{u_{00}} \right)^2 \]  

(2.44)

which can be expressed further in terms of the frequency dependent friction as

\[ \epsilon = \frac{1}{2} \left[ \frac{\overline{\gamma}(\lambda_b)}{\lambda_b} + \frac{\partial \overline{\gamma}(\lambda_b)}{\partial \lambda_b} \right] \]  

(2.45)

Furthermore for future use we also define a parameter

\[ K_c(t) = \sum_{i=1}^{N} \left( \frac{u_{i0}}{u_{00}} \right)^2 \cos(\lambda_i t) \]  

(2.46)

whose Laplace transform is given by

\[ \tilde{K}_c(s) = \frac{1}{u_{00}^2} \frac{s}{s^2 + s \overline{\gamma}(s) - \omega^2_b} - \frac{s}{s^2 - \lambda^2_b} \]  

(2.47)
III. C-NUMBER QUANTUM VERSION OF MULTIDIMENSIONAL TST

To begin with we consider the particle to be trapped in a well described by a potential \( V(q) \) depicted schematically in Fig.1. In the normal mode description of \((N + 1)\) oscillators according to the Hamiltonian (2.31), the bath modes and the system mode are uncoupled. Considering the unstable reaction co-ordinate to be thermalized according to the Wigner thermal canonical distribution of \( N \) uncoupled harmonic oscillators plus one inverted we have

\[
W_{eq} = z^{-1} \exp \left[ -\frac{1}{2} \rho^2 + V_1^\dagger - \frac{1}{2} \lambda_b^2 \rho^2 \right] \prod_{i=1}^{N} \exp \left[ -\frac{1}{2} \lambda_i^2 y_i^2 \right]
\]  

(3.1)

\( z \) is the normalization constant. As usual this can be calculated using the distribution function inside the reactant well. For this it is necessary to consider the normal mode Hamiltonian at the bottom of the well expressed as \( H_0' \) in the Eq.(2.41). The corresponding distribution in the well is

\[
W_{eq} = z^{-1} \exp \left[ -\frac{1}{2} \rho^2 + \frac{1}{2} \lambda_0^2 \rho^2 \right] \prod_{i=1}^{N} \exp \left[ -\frac{1}{2} \lambda_i^2 y_i^2 \right]
\]  

(3.2)

which can be normalized to obtain

\[
z^{-1} = \frac{\lambda_0}{2\pi \hbar \lambda_0 (\pi_0(\lambda_0) + \frac{i}{2})} \prod_{i=1}^{N} \frac{\Lambda_i}{2\pi \hbar \Lambda_i (\pi_i(\Lambda_i) + \frac{i}{2})}
\]  

(3.3)

The identity relation (2.41) can be used to transform (3.3) to the following form

\[
z^{-1} = \frac{\omega_0}{2\pi \hbar \lambda_0 (\pi_0(\lambda_0) + \frac{i}{2})} \prod_{i=1}^{N} \frac{\omega_i}{2\pi \hbar \Lambda_i (\pi_i(\Lambda_i) + \frac{i}{2})}
\]  

(3.4)

Putting Eq. (3.4) in Eq. (3.1) we obtain after integration over the stable modes

\[
W_{eq} = \frac{\omega_0}{2\pi \hbar \lambda_0 (\pi_0(\lambda_0) + \frac{i}{2})} \frac{\lambda_0}{\omega_b} \chi \exp \left[ -\frac{1}{2} \rho^2 + V_1^\dagger - \frac{1}{2} \lambda_b^2 \rho^2 \right]
\]  

(3.5)

where

\[
\chi = \prod_{i=1}^{N} \frac{\hbar \lambda_i (\pi_i(\Lambda_i) + \frac{i}{2})}{\hbar \Lambda_i (\pi_i(\Lambda_i) + \frac{i}{2})}
\]  

(3.6)

The total energy of the unstable mode is

\[
E = \frac{1}{2} \rho^2 + V_1^\dagger - \frac{1}{2} \lambda_b^2 \rho^2
\]  

(3.7)

The prime quantity for determination of rate constant is the distribution of energy of the unstable mode. Thus going over to an energy space so that the co-ordinate \( \rho, \dot{\rho} \) are transformed to \( t, \dot{E} \), respectively with unit Jacobian, the equilibrium distribution function (3.3) is given by,

\[
f_{eq}(E) = \frac{\omega_0}{2\pi \hbar \lambda_0 (\pi_0(\lambda_0) + \frac{i}{2})} \frac{\lambda_0}{\omega_b} \chi \exp \left[ -\frac{E}{\hbar \lambda_0 (\pi_0(\lambda_0) + \frac{i}{2})} \right]
\]  

(3.8)

The above distribution is valid for the energy of the unstable mode \( E > V_1^\dagger \) as well as \( E < V_1^\dagger \).
A. Quantum multidimensional TST rate

The rate of activated barrier crossing in terms of the equilibrium probability becomes

\[ \Gamma = \int_{V^+}^\infty f(E) \, dE \]  \hspace{1cm} (3.9)

As the unstable mode remains uncoupled from the stable modes the former mode behaves deterministically and the recrossing does not occur in this case.

Making use of the distribution (3.8) in (3.9) we obtain the rate constant

\[ \Gamma_{TST} = \frac{\omega_0}{2\pi} \frac{\lambda_b}{\omega_b} \chi \exp \left[ -\frac{V^+}{\hbar \lambda_0 (\lambda_0) + \frac{1}{2}} \right] \] \hspace{1cm} (3.10)

The above expression corresponds to a quantum multidimensional transition state rate constant. This is central result of this section. Apart from usual Kramers’-Grote-Hynes term \( \lambda_b/\omega_b \) and \( \omega_0/2\pi \), the term arising out of classical transition state result, Eq.(3.10) contains two important factors. First, an exponential Arrhenius term where the usual thermal factor \( k_B T \) is replaced by \( \hbar \lambda_0 (\lambda_0) + \frac{1}{2} \) includes quantum effects due to heat bath at very low temperature. In the high temperature limit it reduces to \( k_B T \) and one recovers the usual Boltzmann factor. This term is essentially an offshoot of a description of thermal equilibrium by a canonical Wigner distribution of harmonic oscillators heat bath. Second term \( \chi \) can be identified as the quantum correction to Grote-Hynes factor or more precisely a vacuum corrected generalized Wolynes contribution for quantum transmission and reflection for the finite barrier. While usual Wolynes term takes care of the quantum effects at the higher temperature the factor \( \chi \) incorporates quantum effects at arbitrary low temperature. In what follows we show that the usual Wolynes term can easily be recovered for \( \chi \) in the appropriate limit.

B. Derivation of Wolynes factor from \( \chi \)

We begin by noting that \( n(x) \) in \( \chi \) which is given by

\[ \chi = \prod_{i=1}^{N} \frac{\hbar \lambda_i (\lambda_i) + \frac{1}{2}}{\hbar \lambda_i (\lambda_i) + \frac{1}{2}} \] \hspace{1cm} (3.11)

is the Bose distribution \( n(x) = (e^{\hbar x/k_B T} - 1)^{-1} \). Neglecting the vacuum contribution \( 1/2 \) from the terms like \( \hbar x (\lambda_i) + \frac{1}{2} \) and keeping only the leading order quantum contribution in the thermal limit we obtain

\[ \hbar x \left( n(x) + \frac{1}{2} \right) \approx \frac{\hbar x}{2} \left( \sinh \frac{\hbar x}{2 k_B T} \right)^{-1} \] \hspace{1cm} (3.12)

Therefore \( \chi \) reduces to \( \Xi \) (say) the Wolynes factor

\[ \Xi = \prod_{i=1}^{N} \frac{\lambda_i \left( \sinh \frac{\hbar \lambda_i}{2 k_B T} \right)^{-1}}{\Lambda_i \left( \sinh \frac{\hbar \Lambda_i}{2 k_B T} \right)^{-1}} \] \hspace{1cm} (3.13)

From identities (2.39) and (2.40) it follows

\[ \prod_{i=1}^{N} \lambda_i = \frac{\omega_0}{\lambda_0} \prod_{i=1}^{N} \omega_i \] \hspace{1cm} (3.14)

\[ \prod_{i=1}^{N} \Lambda_i = \frac{\omega_0}{\lambda_0} \prod_{i=1}^{N} \omega_i \] \hspace{1cm} (3.15)
respectively, and we have

\[ N \prod_{i=1}^{N} \frac{\lambda_i}{\Lambda_i} = \frac{\lambda_0 \omega_b}{\omega_0 \lambda_b} \]  

(3.16)

Making use of the relation 3.16 in (3.13) we obtain

\[ \Xi = \frac{\lambda_0 \omega_b}{\omega_0 \lambda_b} \prod_{i=1}^{N} \frac{\sinh(\hbar \Lambda_i/2k_B T)}{\sinh(\hbar \lambda_i/2k_B T)} \]  

(3.17)

Furthermore \((\lambda_0 \omega_b)/(\omega_0 \lambda_b)\) can be rewritten as

\[ \frac{\omega_b}{\omega_0} \frac{\sinh(\hbar \lambda_0/2k_B T)}{\sinh(\hbar \lambda_0/2k_B T)} \frac{\sinh(\hbar \lambda_b/2k_B T)}{\sinh(\hbar \lambda_b/2k_B T)} \]  

which may be approximated in the form

\[ \omega_b \omega_0 \frac{\sinh(\hbar \lambda_0/2k_B T)}{\sinh(\hbar \lambda_0/2k_B T)} \frac{\sinh(\hbar \lambda_b/2k_B T)}{\sinh(\hbar \lambda_b/2k_B T)} \]  

Eq. (3.17) then reduces to

\[ \Xi = \omega_b \omega_0 \frac{\sinh(\hbar \lambda_0/2k_B T)}{\sinh(\hbar \lambda_0/2k_B T)} \prod_{i=1}^{N} \frac{\sinh(\hbar \lambda_i/2k_B T)}{\sinh(\hbar \lambda_i/2k_B T)} \]  

(3.18)

This is the wellknown Wolynes [10, 26] expression derived in early eighties as a higher temperature equilibrium quantum correction to Kramers'-Grote-Hynes dynamical factor to Kramers' rate. Both \(\chi\) and the Wolynes factor become unity in the classical limit. We conclude by noting that unlike Wolynes factor \(\Xi\), \(\chi\) is valid below cross-over temperature.

IV. THE COUPLING BETWEEN THE NORMAL MODES, ENERGY LOSS AND THE QUANTUM RATE

The rate formula (3.9) is quite general and requires the knowledge of \(f(E)\). In the last section the quantum version of Kramers'-Grote-Hynes estimation of this rate rests on the replacement of \(f(E)\) by an equilibrium Wigner distribution function in phase space. A determination of \(f(E)\) from the dynamics of the energy diffusion process, however is based on the solution of the integral equation originally formulated by Melnikov [7] and subsequently by others [9, 12],

\[ f(E) = \int_{0}^{V-1} dE' \ P(E|E') \ f(E') \]  

(4.1)

which implies that \(f(E)\) can be determined by a conditional probability function \(P(E|E')\) \(dE\) that a system escaping the barrier region with energy \(E'\) of the unstable mode makes a round trip of the barrier with an energy between \(E\) and \(E + dE\). Deep inside the well, the strong coupling between the stable and unstable modes brings \(f(E)\) close to its equilibrium value \(W_{eq}\), whereas a weak coupling prevails where the energy is close to the barrier energy. A detailed consideration of this weak coupling between the stable and unstable modes results in the conditional probability function \(P(E|E')\) which when made use in (4.1) gives the rate constant beyond the multidimensional TST limit.

To proceed further we construct the equation of motion for the normal modes corresponding to the Hamiltonian (2.31) using (2.26) and (2.34).

\[ \ddot{\rho} - \lambda_0^2 \rho = -u_{00} V_N'(u_{00} \rho + \sum_{i=1}^{N} u_{i0} y_i) \]  

(4.2)

\[ \ddot{y}_i + \lambda_i^2 y_i = -u_{i0} V_N'(u_{00} \rho + \sum_{i=1}^{N} u_{i0} y_i) \]  

(4.3)

where \(V_N'\) denotes the derivative of \(V_N(x)\) with respect to \(x\). An important point is noteworthy. In contrast to classical theories where \(V_N\) is purely an anharmonic classical contribution, \(V_2\), the present treatment incorporates quantum effects due to nonlinearity of the system potential \(V_3\) entangled with quantum dispersion terms as given in Eq. (2.28). Since the coupling between the stable and unstable normal modes is very sensitive to the small variation of
energy we expect the quantum effect to contribute significantly to the energy loss mechanism and hence the calculation of depopulation factor. This is an important point of departure from the earlier treatment of Rips and Pollak who had considered the unstable mode to be classical and neglected this contribution. The applicability of the theory is thus not restricted to so-called activated tunneling region only.

Defining a smallness parameter \( g_i = u_{i0}/u_{00} \) and \( \epsilon = \sum g_i^2 \) we may write the zero order equation of motion for the unstable mode as

\[
\ddot{\rho} - \lambda_i^2 \rho = -u_{00} V'_N(u_{00} \rho) \tag{4.4}
\]

and for the stable modes as

\[
\ddot{y}_i + \lambda_i^2 y_i = g_i \zeta \tag{4.5}
\]

where \( \zeta \) is a forcing function given by

\[
\zeta(t) = -u_{00} V'_N(u_{00} \rho) \tag{4.6}
\]

The parameter \( \epsilon \ll 1 \) is for weak coupling. The forcing function \( \zeta(t) \) can be determined by the unperturbed motion of the unstable mode \( \rho \). The general solution of Eq. (4.5) is given by

\[
y_i(t) = y_i(0) \cos(\lambda_i t) + \frac{\dot{y}_i(0)}{\lambda_i} \sin(\lambda_i t) + \int_0^t dt' \frac{\sin(\lambda_i(t-t'))}{\lambda_i} g_i \zeta(t') \tag{4.7}
\]

As noted earlier that at equilibrium the initial distribution of the stable normal modes \( y_i(0) \) and \( \dot{y}_i(0) \) is a thermal canonical Wigner distribution so that

\[
\langle y_i(0) \rangle_S = \langle \dot{y}_i(0) \rangle_S = \langle y_i(0) \dot{y}_i(0) \rangle_S = 0
\]

\[
\langle \dot{y}_i(0)^2 \rangle_S = \lambda_i^2 \langle y_i(0)^2 \rangle_S = \hbar \lambda_i \left( \pi_i(\lambda_i) + \frac{1}{2} \right) \tag{4.8}
\]

The total c-number energy of the stable bath modes during the traversal of \( \rho \) mode over a round trip time \( t_p \),

\[
E = \sum_{i=1}^{N} E_i = \sum_{i} \frac{1}{2} \dot{y}_i^2 + \frac{1}{2} \lambda_i^2 y_i^2 \tag{4.9}
\]

can be calculated from (4.7) and may be put in the form

\[
E = E' - \Delta E + \delta E \tag{4.10}
\]

\( E' = \sum_i E_i(0) \) where \( E_i(0) \) is the initial energy of the i-th bath oscillator. The gain of energy by the stable modes is equal to the loss of energy of the unstable mode. This is characterized by a systematic and a stochastic contribution to energy loss of the unstable mode \( \Delta E \) and \( \delta E \), respectively. These are given by

\[
\Delta E = \frac{1}{2} \sum_{i=1}^{N} g_i^2 \int_0^{t_p} dt \int_0^{t_p} dt' \cos[ \lambda_i(t-t') ] \zeta(t) \zeta(t') \tag{4.11}
\]

\[
\delta E = \sum_{i=1}^{N} g_i \int_0^{t_p} dt \left[ \dot{y}_i(0) \cos(\lambda_i t) - y_i(0) \lambda_i \sin(\lambda_i t) \right] \zeta(t) \tag{4.12}
\]

While \( \Delta E \) represents a systematic energy loss due to coupling, \( \delta E \) is a measure of instantaneous loss induced by Gaussian fluctuation around \( \langle E \rangle = E' - \Delta E \) such that
\[
\langle \delta E \rangle = 0 \quad \text{and} \quad \langle \delta E^2 \rangle = D
\] (4.13)

Making use of the relation (4.8), \( \langle \delta E^2 \rangle \) can be calculated as
\[
\langle \delta E^2 \rangle = \sum_{i=1}^{N} q_i^2 \int_{0}^{t_p} dt \int_{0}^{t_p} dt' \ h\lambda_i \ \left[ \eta_i(t) + \frac{1}{2} \right] \ \cos[\lambda_i(t - t')] \ \zeta(t) \ \zeta(t')
\] (4.14)

In the Markovian limit (4.14) reduces to
\[
\langle \delta E^2 \rangle = 2 \ h\lambda_b \ \left[ \eta_b + \frac{1}{2} \right] \ \Delta E
\] (4.15)

The mean and the second moments of the energy fluctuations lead us to the conditional distribution function of the Gaussian form as
\[
P(E|E') = \frac{1}{\sqrt{2\pi D}} \ \exp \left[ - \frac{(E - E' + \Delta E)^2}{2D} \right]
\] (4.16)

The Markovian limit of the above expression can be obtained by replacing \( D \) by (4.15).

We now proceed to calculate the rate explicitly. As is well known that as probability function \( f(E) \) tends to its equilibrium limit \( W_{eq} \) the rate \( \Gamma \) reduces to the rate calculated by multidimensional transition state theory. If, in general, they differ by a depopulation factor \( f_T \) as defined in
\[
\Gamma = f_T \ \frac{\omega_0}{2\pi} \ \frac{\lambda_b}{\omega_b} \ \exp \left[ - \frac{V^\dagger}{h\lambda_0(\eta_0(\lambda_0) + \frac{1}{2})} \right]
\] (4.17)

so that by comparing (4.17) with (3.9) to include all energies we write
\[
f_T = \frac{2\pi}{\omega_0} \ \frac{1}{\chi} \ \frac{\omega_b}{\lambda_b} \ \exp \left[ \frac{V^\dagger}{h\lambda_0(\eta_0(\lambda_0) + \frac{1}{2})} \right] \ \int_{0}^{\infty} f(E) \ dE
\] (4.18)

Introducing one-sided Fourier transformation ansatz as
\[
\phi^+(\lambda) = \frac{2\pi}{\omega_0} \ \frac{1}{\chi} \ \frac{\omega_b}{\lambda_b} \ \exp \left[ \frac{V^\dagger}{h\lambda_0(\eta_0(\lambda_0) + \frac{1}{2})} \right] \ \times \ \int_{0}^{\infty} f(E) \ \exp \left[ \frac{2(i\lambda + 1/2)\Delta E E}{D} \right] \ dE
\] (4.19)

and
\[
\phi^-(\lambda) = \frac{2\pi}{\omega_0} \ \frac{1}{\chi} \ \frac{\omega_b}{\lambda_b} \ \exp \left[ \frac{V^\dagger}{h\lambda_0(\eta_0(\lambda_0) + \frac{1}{2})} \right] \ \times \ \int_{-\infty}^{0} f(E) \ \exp \left[ \frac{2(i\lambda + 1/2)\Delta E E}{D} \right] \ dE
\] (4.20)

it is possible to transform (4.17) into Wiener-Hopf [7, 12, 35, 36] equation with symmetric kernel which can be solved by standard technique first suggested by Melnikov and Meshkov in the rate theoretical context and subsequently used by others. The ultimate expression of rate can be worked out as
the quantum depopulation factor is essentially due to the weak coupling of the c-number unstable normal mode with the stable modes at the barrier top. This quantity signifies the nonequilibrium nature of the dynamics at the barrier top and depends on the average energy loss of the c-number unstable mode as well as on the energy dispersion. Since both of them are sensitive to the coupling, we emphasize that the quantum effect due to nonlinearity of the system makes its presence felt in these quantities. Apart from these couplings, quantum nature of the system is also manifested in $t_p$, the round-trip time, for a complete traversal in the well. The latter point can be understood more explicitly as we go over to Section VI.

Before closing this section we point out that (i) because of low temperature quantum correction to Kramers’-Grote-Hynes factor, the quantum nature of the unstable mode, and a Wigner description of probability distribution inside the well, the rate expression is valid both above and below the crossover temperature. Thus this works well below the so-called activated tunneling regime down to vacuum limit. (ii) Since in this present calculation the dissipation effects are not restricted to Markovian limit, the rate expression is valid for arbitrary frequency-dependent friction. (iii) Finally from the expressions for the two primary quantities that determine the quantum depopulation factor, i.e., the average energy loss $\Delta E$ and energy dispersion $\langle \delta E^2 \rangle$ it is apparent that the classical limit of the depopulation factor can be recovered by reducing these two quantities in the limit $k_B T \gg \hbar \lambda_0$ and neglecting quantum correction in $V_0$. The result is the classical depopulation factor \[ \text{(4.2)} \] (iv) An important advantage of the present c-number scheme is that it allows us to use a Gaussian kernel which is exactly classical in form (as used by Melnikov and Meshkov) but quantum mechanical in its content since the energy loss $\Delta E$ and the dispersion $\langle \delta E^2 \rangle$ are quantum mechanical in character. The quantum-classical correspondence thus be immediately restored. The rate expression \[ \text{(4.21)} \] reduces to its classical non-Markovian expression at high temperature where $\hbar x(\pi(x) + 1/2)$ becomes $k_B T$ so that the Wolynes factor $\chi$ goes over to unity and the depopulation factor takes its classical value. We obtain the expression for Pollak-Grabert-Hänggi as follows:

\[
\Gamma = \frac{\omega_0}{2\pi} \frac{\lambda_b}{\omega_b} \times \exp \left[ -\frac{V \dagger}{\hbar \lambda_0(\lambda_0) + \frac{1}{2}} \right] \\
\times \exp \left[ \frac{1}{2\pi} \int_{-\infty}^{\infty} \ln[1 - \exp(-\frac{2\Delta E^2}{\lambda^2 + 1/4})] d\lambda \right]
\]

\[(4.21)\]

This is the central result of the paper. The quantum rate is a product of several terms. The first term corresponds to classical well frequency factor according to transition state theory. The second is the classical Kramers’-Grote-Hynes factor for arbitrary frequency dependent friction. The third term $\chi$ as given by \[ \text{(4.10)} \] corresponds to equilibrium quantum correction to Kramers’-Grote-Hynes factor which reduces to high temperature quantum correction or Wolynes term in the appropriate limit as shown in Sec.III. The fourth term refers to the Wigner’s canonical thermal distribution in the harmonic well and reduces to the usual Arrhenius factor in the classical limit when $\hbar \lambda_0(\pi_0(\lambda_0) + \frac{1}{2}) \rightarrow k_B T$ for $\hbar \lambda_0 \ll k_B T$. This term takes care of the quantum effects of the heat bath which thermalizes the particle inside the well. The vacuum term \[ \text{1} \] prevents the distribution from being singular as one approaches to absolute zero. Therefore a significant contribution of quantum correction due to heat bath to the rate enters through both equilibrium Wigner function and $\chi$. The last term, the quantum depopulation factor is essentially due to the weak coupling of the c-number unstable normal mode with the stable modes at the barrier top. This quantity signifies the nonequilibrium nature of the dynamics at the barrier top and depends on the average energy loss of the c-number unstable mode as well as on the energy dispersion. Since both of them are sensitive to the coupling, we emphasize that the quantum effect due to nonlinearity of the system makes its presence felt in these quantities. Apart from these couplings, quantum nature of the system is also manifested in $t_p$, the round-trip time, for a complete traversal in the well. The latter point can be understood more explicitly as we go over to Section VI.

V. THE QUANTUM CORRECTION TO ENERGY LOSS OF THE UNSTABLE MODE

The key issue in Kramers’ turnover problem is the calculation of energy loss $\Delta E$ of the unstable mode during its round trip in the well over a time $t_p$. This is extremely sensitive to coupling of the stable and the unstable modes described in terms of the equations of motion for the normal modes \[ \text{(4.12)} \] and \[ \text{(4.13)} \]. The present calculation by virtue of considering the quantum system mode takes care of this loss through $\zeta(t)$ or through the nonlinearity of the system potential $V_N$. Furthermore the time $t_p$ depends explicitly on the quantum corrections as may be seen in the next section. Thus the quantum corrections $B_n$ (in Eq. \[ \text{(2.24)} \]) are the key quantities that need to be determined. In an illustrative example of the next section with a cubic potential, we show that $B_2$ is the relevant quantity for the leading
order quantum correction. In the following we give a recipe for calculation of quantum corrections. We return to the operator equation (2.2) and put (2.19) and (2.20) to obtain

\[ \dot{\delta q} = \delta \dot{p} \]  

(5.1)

\[ \delta \dot{p} + \int_0^t \gamma(t-t') \delta \dot{p}(t') \, dt' + V''(q) \delta q \]

+ \sum_{n \geq 2} \frac{1}{2} V^{(n+1)}(q) (\langle \delta q^n \rangle - \langle \delta q^n \rangle) = \hat{F}(t) - f(t) \]

(5.2)

We then perform a quantum mechanical averaging over bath states with \( \prod_{i=1}^N \langle \alpha_i(0) \rangle \) to get rid of the term \( \hat{F}(t) - f(t) \). The Eqs. (5.1) and (5.2) along with (2.16) and (2.17) form the key element for calculation of the quantum mechanical correction due to the nonlinearity of the potential. Considering the friction kernel \( \gamma(t) \) to be arbitrary (but decaying) we may calculate the leading order quantum correction for the harmonic mode at the barrier top for which higher derivatives of \( V(q) \) in (5.2) vanish. The above equations can then be solved by Laplace transformation technique to obtain

\[ \delta \dot{q}(t) = \delta \dot{p}(0) \, C_v(t) + \left( 1 + \omega_b^2 \int_0^t C_v(t') \, dt' \right) \delta \dot{q}(0) \]

(5.3)

and

\[ \delta \dot{p}(t) = \delta \dot{p}(0) \, C_v(t) + \delta \dot{q}(0) \, C_q(t) \]

(5.4)

where

\[ C_v(t) = L^{-1} \left[ \frac{1}{s^2 + s \tilde{\gamma}(s) - \omega_b^2} \right] \]

(5.5)

and

\[ C_q(t) = 1 + \omega_b^2 \int_0^t C_v(t') \, dt' \]

(5.6)

and \( \tilde{\gamma}(s) \) is the Laplace transform of \( \gamma(t) \) defined as \( \tilde{\gamma}(s) = \int_0^\infty \gamma(t) e^{-st} \, dt \). After squaring and quantum mechanical averaging Eq. (5.3) yields

\[ \langle \delta q^2(t) \rangle = \langle \delta \dot{p}^2(0) \rangle C_v^2(t) + \langle \delta \dot{q}^2(0) \rangle C_q^2(t) \]

+ \[ C_v(t) \, C_q(t) \langle \delta \dot{p}(0) \, \delta \dot{q}(0) \rangle \]

(5.7)

The relevant quantum correction in \( V_N \) in the leading order is \( B_2 \) obtained as a time average of \( \langle \delta \dot{q}^2(t) \rangle \).

\[ B_2 = \frac{1}{t_p} \int_0^{t_p} \langle \delta \dot{q}^2(t) \rangle \, dt \]

(5.8)

While for Markovian friction, the above equation can be calculated analytically, one must take resort to numerical evaluation of \( C_v(t) \) and \( C_q(t) \) for arbitrary friction kernel. We emphasize that the correction \( B_2 \) is the leading order quantum correction for the unstable mode and the friction kernel is considered to be arbitrary in nature. Thus the quantum correction due to the unstable mode affects \( \langle \delta E^2 \rangle \) as well as \( \Delta E \) through \( t_p \) and \( \zeta(t) \). The quantum nature of the heat bath on the other hand is taken care of through the width parameter of the Wigner canonical thermal distribution function. It is pertinent to mention at this point that the quantum correction to the average energy loss and dispersion of energy can be calculated by including higher order contribution with the help of the basic equations (5.1) and (5.2) within the framework of the theory. However, the coupling of the unstable and the stable modes at the barrier top being weak it is sufficient to consider this leading order quantum correction for the present treatment.
VI. APPLICATION TO A CUBIC OSCILLATOR

The theory developed so far is fairly general in the sense that it takes into account of an arbitrary form of nonlinear potential \( V(q) \) and a frequency dependent friction. We now consider a simple nonlinear potential of the form chosen for comparison with standard results \([9, 10]\)

\[
V(q) = -aq^3 - bq^2 + \frac{4b^3}{27a^2} \tag{6.1}
\]

The extrema of the potential corresponds to \( q = 0 \) and \( q = (-q_0) = -2b/3a \), the respective potentials being \( 4b^3/27a^2 \) and 0 respectively. Thus we have

\[
V^\dagger = \frac{4b^3}{27a^2}, \quad \omega_0^2 = 2b, \quad \omega_b^2 = 2b \tag{6.2}
\]

the metastable minima is at \( q = -q_0 \). Furthermore we assume a Lorentian form of spectral density function, \( J(\omega) \) as

\[
J(\omega) = \frac{\omega \gamma_1 + \omega^2 \gamma_2}{\omega^2 \gamma^2 \tau_c^2} \tag{6.3}
\]

for which the friction kernel has an exponential form as

\[
\gamma(t) = \frac{1}{\tau_c} \exp\left(-\frac{t}{\gamma \tau_c}\right) \tag{6.4}
\]

The Laplace transform of \( \gamma(t) \) is given by

\[
\tilde{\gamma}(s) = \gamma/(1 + s \gamma \tau_c) \tag{6.5}
\]

We follow the classical procedure of Straub, Borkovec and Berne \([13, 14]\) to consider the potential \((6.1)\) in the form of a piecewise continuous harmonic potential as

\[
V(q) \approx \frac{1}{2} \omega_0^2 (q + q_0)^2 \quad \text{for} \quad q < -q^* \tag{6.6}
\]

\[
\approx V_a^\dagger - \frac{1}{2} \omega_b^2 q^2 \quad \text{for} \quad q \geq -q^* \tag{6.7}
\]

From the continuity of the potential \( V(q) \) and its derivatives at \( q = -q^* \), i.e., \( 1/2 \omega_0^2 (q + q_0)^2|_{-q^*} = V_a^\dagger - 1/2 \omega_b^2 q^2|_{-q^*} \) and \( \omega_0^2 (q + q_0)|_{-q^*} = -\omega_b^2 q|_{-q^*} \) we obtain

\[
V_a^\dagger = \frac{2b^3}{9a^2} \quad \text{and} \quad q^* = -\frac{b}{3a} \tag{6.8}
\]

Now the nonlinearity of the potential around \( q = 0 \) can be estimated from the general expression \((2.28)\) and \((6.1)\). Thus we have

\[
V_N = V_2(q) + V_3(q) \tag{6.9}
\]

\[
= \sum_{n \geq 3} \frac{1}{n!} V^{(n)}(q)|_{q=0} q^n + \sum_{n \geq 2} \frac{B_n}{n!} V_2^{(n)}(q)
\]

\[
= -a q^3 - 3B_2 a q - B_3 a \tag{6.10}
\]

where \( B_2 \) and \( B_3 \) defined in \((2.25)\), are the quantum corrections to the potential due to nonlinearity. The details of the evaluation of \( B_n \) are given in Sec.V. Linearizing \( V_N \) around \( q = -q_0 \) we obtain the nonlinear part of the potential.
\[ V_N(q) \approx (3a q_0) q^2 + (3a q_0^2 - 3a B_2) q + (a q_0^3 - a B_3) \]  
(6.11)

and its derivative

\[ V'_N(q) = (6a q_0) q + (3a q_0^2 - 3a B_2) \]  
(6.12)

We are now in a position to write down the equation motion (4.4) for the unstable mode explicitly for the potential concerned for the present problem

\[ \ddot{\rho} - \lambda_0^2 \rho = - \left[ (4b u_{60}^2) \rho + \left( \frac{4b^2}{3a} u_{60}^2 - 3a B_2 \right) \right] \]  
(6.13)

or in the following form

\[ \ddot{\rho} + \lambda_0^2 \rho = r \]  
(6.14)

where \( \lambda_0^2 = 4b u_{60}^2 - \lambda_0^2 \)  
(6.15)

and \( r = \left( \frac{4b^2}{3a} u_{60}^2 - 3a B_2 \right) \)  
(6.16)

If the unstable mode start moving at \( -\rho^* \) with total energy \( V^* \), then the initial value of the momentum for the unstable normal mode is

\[ \dot{\rho}(t = 0) = -\frac{1}{u_{00}} \left( \frac{b \lambda_0}{3a} \right) \]  
(6.17)

The corresponding unstable co-ordinate is

\[ \rho(t = 0) = -\frac{1}{u_{00}} \left( \frac{b}{3a} \right) \]  
(6.18)

For a round trip, the time elapsed is \( t_p \); we have

\[ \rho(t = t_p) = -\frac{1}{u_{00}} \left( \frac{b}{3a} \right) \]  
(6.19)

\[ \text{and} \quad \dot{\rho}(t = t_p) = \frac{1}{u_{00}} \left( \frac{b \lambda_0}{3a} \right) \]  
(6.20)

The equation for the unstable mode (6.13) can be solved to obtain

\[ \rho(t) = M \cos(\lambda_0 t) + N \sin(\lambda_0 t) + \frac{r}{\lambda_0^2} \]  
(6.21)

where \( M \) and \( N \) are given by

\[ M = -\left( \frac{b}{3a u_{00}} + \frac{r}{\lambda_0^2} \right), \quad N = -\frac{1}{\lambda_0 u_{00}} \left( \frac{b \lambda_0}{3a} \right) \]  
(6.22)
The round trip time \( t_p \) can be calculated from Eq. (6.21) and its derivative equation for \( \rho \) and applying the conditions (6.19) and (6.20) on them so that we have

\[
\cos(\lambda_0 t_p) = \frac{M^2 - N^2}{M^2 + N^2}, \quad \sin(\lambda_0 t_p) = \frac{2MN}{M^2 + N^2}
\]  

(6.23)

Here we also note the range of \( t_p \) as \( \pi < \lambda_0 t_p < 2\pi \). An important point to emphasize is that \( t_p \) contains a quantum correction.

In order to calculate the energy loss due to the unstable mode we now return to Eq. (4.11) so that we write it as

\[
\Delta E = \frac{1}{2} \int_0^{t_p} dt \int_0^{t_p} dt' K_c(t - t') \zeta(t) \zeta(t')
\]  

(6.24)

where \( K_c(t) \) has the form given by Eq. (2.46) since \( g^2_{ii} = \left( \frac{u_{i0}}{u_{00}} \right)^2 \)

Since \( \tilde{\gamma}(s) \) is given by (6.5), \( K_c(t) \) can be calculated explicitly using (2.47) as in the classical theory [9] to obtain

\[
K_c(t) = \frac{1}{2} \exp(-\xi t) \left[ (1 + 2\epsilon) \cosh(\sigma t) + \frac{(1 + 2\epsilon)\xi - \lambda_b}{\sigma} \sinh(\sigma t) \right]
\]  

(6.25)

where \( \xi \) and \( \sigma \) are defined as

\[
\xi = \frac{1}{2} (\lambda_b + 1/(\gamma \tau_c)) \quad \text{and} \quad \sigma^2 = \xi^2 - \omega_b^2/(\gamma \tau_c \lambda_b).
\]

\( \zeta(t) \) is given by (4.6) and using (6.12) we obtain explicitly

\[
\zeta(t) = -4b u_{00}^2 \rho(t) - \left( \frac{4b^2 u_{00}^2}{3a} - 3aB_2 \right)
\]  

(6.26)

We then make use of the solution (6.21) for \( \rho(t) \) in (6.26) to obtain

\[
\zeta(t) = M_1 \cos(\lambda_0 t) + N_1 \sin(\lambda_0 t) - P
\]  

(6.27)

where

\[
\begin{align*}
M_1 &= -4Mbu_{00}^2 \\
N_1 &= -4Nb^2u_{00} \\
P &= \frac{4b^2 u_{00}^2 r}{\lambda_0^2} + \frac{4b^2 u_{00}^2}{3a} - 3aB_2
\end{align*}
\]  

(6.28)

We are now in a position to calculate the energy loss \( \Delta E \) of the unstable mode using (6.24) from (6.25) and (6.27). After a little bit of algebra we obtain

\[
\Delta E = \frac{1 + 2\epsilon}{8} \left[ R(\xi + \sigma) + R(\xi - \sigma) \right] - \frac{(1 + 2\epsilon)\xi - \lambda_b}{8\sigma} \left[ R(\xi + \sigma) - R(\xi - \sigma) \right] - \frac{1}{4} R(\lambda_b)
\]  

(6.29)

where

\[
R(z) = \int_0^{t_p} dt \int_0^{t_p} dt' e^{-z(t-t')} \left[ M_1 \cos(\lambda_0 t) + N_1 \sin(\lambda_0 t) - P \right] \times \left[ M_1 \cos(\lambda_0 t') + N_1 \sin(\lambda_0 t') - P \right]
\]  

(6.30)

Explicit evolution of the integrals in (6.30) yields
Our next task is to calculate the width \( D \) of the distribution function (4.16). \( D \) is defined in (4.14) (and (4.13)) and we now rewrite
\[
\langle \delta E^2 \rangle = \int_0^{t_p} dt \int_0^{t_p} dt' K_Q(t-t') \zeta(t) \zeta(t')
\] (6.32)
where
\[
K_Q(t) = \sum_{i=1}^{N} g_i^2 \hbar \lambda_i \left( \frac{n_i}{2} + 1 \right) \cos(\lambda_i t)
\] (6.33)
We also recall Eq. (2.46)
\[
K_c(t) = \sum_{i=1}^{N} g_i^2 \cos(\lambda_i t)
\] (6.34)
By going over to continuum modes \( K_c(t) \) and \( K_Q(t) \) can be expressed as
\[
K_Q(t) = \int_0^{\infty} d\lambda \; g^2(\lambda) f(\lambda) J(\lambda) \cos(\lambda t)
\] (6.35)
and
\[
K_c(t) = \int_0^{\infty} d\lambda \; g^2(\lambda) J(\lambda) \cos(\lambda t)
\] (6.36)
where \( f(\lambda) = \frac{1}{2} \hbar \lambda \coth(\hbar \lambda / 2k_B T) \). It can be easily shown that the above two quantities can be related in the Fourier transform domain as
\[
\tilde{K}_Q(\lambda) = f(\lambda) \tilde{K}_c(\lambda)
\] (6.37)
Here \( \tilde{K}_Q(\lambda) \) and \( \tilde{K}_c(\lambda) \) are the cosine transform of \( K_Q(t) \) and \( K_c(t) \) respectively.
\[
\tilde{K}_c(\lambda) = \left( \frac{2}{\pi} \right)^{1/2} \int_0^{\infty} dt \; K_c(t) \cos(\lambda t)
\] (6.38)
Making use of the expression \( K_c(t) \) from Eq. (6.25) in Eq. (6.38), followed by a multiplication of \( f(\lambda) \), yields \( \tilde{K}_Q(\lambda) \). The inverse transform of \( \tilde{K}_Q(\lambda) \) finally gives
\[ K_Q(t) = \left( \frac{2}{\pi} \right)^{1/2} \int_0^\infty d\lambda \frac{\lambda}{2} \coth \left( \frac{\hbar \lambda}{2k_BT} \right) \cos(\lambda t) \times \left[ \frac{W_1}{(\xi + \sigma)^2 + \lambda^2} + \frac{W_2}{(\xi - \sigma)^2 + \lambda^2} - \frac{W_3}{\lambda_b^2 + \lambda^2} \right] \]  

(6.39)

Here

\[ W_1 = \left( \frac{2}{\pi} \right)^{1/2} \left\{ \frac{1 + 2\epsilon}{4} - \frac{(1 + 2\epsilon)\xi - \lambda_b}{4\sigma} \right\} (\xi + \sigma) \]
\[ W_2 = \left( \frac{2}{\pi} \right)^{1/2} \left\{ \frac{1 + 2\epsilon}{4} + \frac{(1 + 2\epsilon)\xi - \lambda_b}{4\sigma} \right\} (\xi - \sigma) \]
\[ W_3 = \left( \frac{2}{\pi} \right)^{1/2} \frac{\lambda_b}{2} \]

(6.40)

with (6.29) and (6.39) we obtain the expression for \( \langle \delta E^2 \rangle \) as follows.

\[ \langle \delta E^2 \rangle = D \]
\[ = \left( \frac{1}{2\pi} \right)^{1/2} \frac{\hbar}{\lambda} \int_0^\infty d\lambda \lambda \coth \left( \frac{\hbar \lambda}{2k_BT} \right) \times \left[ \frac{W_1}{(\xi + \sigma)^2 + \lambda^2} + \frac{W_2}{(\xi - \sigma)^2 + \lambda^2} - \frac{W_3}{\lambda_b^2 + \lambda^2} \right] \]
\[ \times \int_0^{t_d} dt \int_0^{t_d} dt' \cos[\lambda(t - t')]\zeta(t)\zeta(t') \]  

(6.41)

The quantum expression of the depopulation factor in Eq. (4.21) primarily depends on the average quantum energy loss \( \Delta E \) and dispersion \( \langle \delta E^2 \rangle \). The expressions of these two quantities have been given in Eq. (6.29) and Eq. (6.41) for a cubic oscillator. An explicit evaluation of these quantities for calculation of the rate or depopulation factor requires numerical calculation. The parameter space chosen for illustration of the main results depicted in Figs.2-5 is based on the earlier work by Pollak et al [9], Rips and Pollak [10], Straub et al [12] for a comparative study. The results are given below.

In Fig.2 we exhibit the quantum turnover by plotting the quantum rate, \( \Gamma/\Gamma_Q \), where \( \Gamma_Q = (\omega_0/2\pi)\chi \exp[\hbar/\lambda_0(\lambda_0 + \lambda_2)] \), as a function of dissipation parameter \( \gamma \) at three different temperatures \( k_BT = 5.0 \) (dotted line) and \( k_BT = 1.0 \) (dashed line) and \( k_BT = 0.0 \) (solid line) for a model potential with \( V^* = 20.0 \), \( a = 0.03042 \), \( b = 0.5 \). The calculation here has been carried out with a non-Markovian friction kernel for \( \tau_c = 1.333 \) and the quantum correction has been taken up to second order. In order to allow ourselves a fair comparison with classical non-Markovian theory of Pollak, Grabert and Hänggi, we compare the quantum (solid line) curves with the corresponding classical (dotted line) curves at two different temperatures \( k_BT = 1.0 \) and \( k_BT = 2.0 \) in Fig.3 for the same set of parameter values as in Fig.2. The following two points are noteworthy. We observe (Fig.2) in conformity with the earlier observation [11, 23] that as the temperature is lowered the maximum at which the quantum turnover occurs shifts to the left and the damping region that corresponds to classical energy diffusion regime becomes exponentially small as one approaches to absolute zero. Second, we observe that the strong friction tends to make the dynamics more classical since the quantum correction is suppressed by dissipation in this regime. On the other hand differential behaviour of the rate in the classical and quantum regime is felt at weak friction regime. This is in confirmation with earlier observations. In Figs.4 and 5 we show a comparison of the quantum rate, \( \Gamma/\Gamma_Q \), calculated on the basis of the present theory (solid line) with that of Rips and Pollak (dotted line) for \( V^* = 26.188 \), \( a = 0.0266 \) and \( b = 0.5 \) at two different scaled temperatures \( k_BT = 1.788 \) and \( k_BT = 2.617 \) respectively in the Markovian limit. The agreement is found to be quite satisfactory. Thus although the depopulation factor in the rate expression \( \rho \) apparently differs in form from that of Pollak and Rips based on quantum transition probability obtained from the solution of master equation, the good numerical agreement between them can not be overlooked (since the remaining factor in \( \Gamma/\Gamma_Q \), the Grote-Hynes factor is same in both the expressions). Figs.4 and 5 therefore serve as a consistency check of the present calculation.
VII. SUMMARY AND CONCLUSION

Based on a quantum Langevin equation we have constructed a c-number Hamiltonian for a system plus N-oscillator bath model. This allows us to formulate a normal mode analysis to realize a c-number version of the multidimensional transition state theory and to derive a quantum expression for the total decay rate of metastable state. The result is valid for arbitrary damping strength and noise correlation and temperature down to vacuum limit. The theory is illustrated on a cubic potential with non-Ohmic dissipation. The following pertinent points are noteworthy.

(i) We have shown that the expression for quantum rate coefficient is a product of five terms, e.g., classical well frequency, Kramers’-Grote-Hynes factor, a vacuum corrected or generalized Wolynes factor representing quantum transmission and reflection, an exponential term corresponding to Wigner canonical thermal distribution i.e., the generalized Arrhenius term and a quantum depopulation factor. Of these the Wigner term and the vacuum corrected Wolynes term refer to equilibration of quantum particle in the well and therefore corresponds to a c-number multi-dimensional transition state result. Since the distribution unlike the Boltzmann is valid even as $T \to 0$, the quantum effect due to heat bath can be well accounted by these terms even below the activated tunneling regime.

(ii) The quantum depopulation factor has a form which is very much similar to its classical counterpart, although intrinsically the relevant quantities determining this factor, i.e., the average quantum energy loss and dispersion are quantum mechanical in their content.

(iii) The classical limit of the quantum rate expression depends on Wigner, generalized Wolynes and depopulation factors. It is easy to see that they reduce to Arrhenius factor, unity and classical depopulation factor, respectively in the limit $\hbar \omega \ll k_B T$.

(iv) Since the quantization of the nonlinear system mode adds an additional contribution to depopulation factor arising out of the weak coupling between the unstable mode and the stable modes the rate is significantly modified.

(v) The theory takes into account of the quantum effects in full due to heat bath, while the quantum correction due to nonlinearity of the system potential can be calculated systematically order by order to a good degree of accuracy. In the illustrative example with cubic potential we have considered the quantum correction of the second order.

(vi) The quantum depopulation factor interpolates the energy diffusion limited regime to spatial diffusion regime and depicts the correct turnover scenario down to absolute zero. The maximum of the turnover shifts to the low damping regime as one approaches the absolute zero. The quantum rate is significantly enhanced over the classical rate in the weak damping regime while strong dissipation overwhelms the quantum correction.

(vii) An important aspect of the present theory is that it takes care of activation and tunneling within a unified description and is equipped to deal with the rate at temperature down to vacuum limit. This is a distinct advantage over path integral Monte Carlo method since numerically the relevant propagator poses serious problem as the temperature approaches absolute zero.

(viii) The present theory is a synthesis of the classical formalism of normal mode analysis and weak coupling theory of unstable and stable modes for calculation of average energy loss and dispersion within the framework of our recently developed c-number quantum Langevin equation. It is important to emphasize a distinct advantage of the present treatment. The present c-number formalism allows us to formulate the Gaussian transition probability that the energy of the unstable mode changes for one period of motion within a ”classical-like” prescription, rather than by solving a quantum master equation restricted to a Markovian description.

The quantum turnover theory as presented here is based on a canonical quantization procedure and positive definite Wigner’s thermal distribution for harmonic oscillators rather than path integral or master equation formalism. It can be readily applied to other models, e.g., a double well oscillator and to the problems of dephasing and related issues. The systematic improvement can be made by taking care of the quantum corrections of higher orders.
Acknowledgement
We are thankful to Dr. B. C. Bag for discussions. The authors are indebted to the Council of Scientific and Industrial Research for partial financial support under Grant No. 01/(1740)/02/EMR-II.

[1] H. A. Kramers, Physica 7 (1940) 284.
[2] E. W.-G. Diau, J.L. Herek, Z.H. Kim and A.H. Zewail, Science 279 (1998) 874.
[3] A. W. Castelman, D.E. Folmer and E.S. Wisniewski, Chem. Phys. Letts. 287 (1998) 1.
[4] K. Luther, J. Schroeder, J. Troe and U. Unterberg, J. Phys. Chem. 84 (1980) 3072.
[5] G. Maneke, J. Schroeder, J. Troe and F. Voss, Ber. Bunsenges. Phys. Chem. 89 (1985) 896.
[6] B. Otto, J. Schroeder and J. Troe, J. Chem. Phys. 81 (1984) 202.
[7] V. I. Melnikov and S.V. Meshkov, J. Chem. Phys. 85(2) (1986) 3271.
[8] V. I. Melnikov, Phys. Reps. 209 (1991) 1.
[9] E. Pollak, H. Grabert and P. Hänggi, J. Chem. Phys. 91 (1989) 4037.
[10] I. Rips and E. Pollak, Phys. Rev. A 41 (1990) 5366.
[11] P. Hänggi, P. Talkner and M. Borkovec, Rev. Mod. Phys. 62 (1990) 251.
[12] W. T. Coffey, D. A. Garanin and D. J. McCarthy, Adv. Chem. Phys. 117 (2001) 483.
[13] J. E. Straub, M. Borkovec and B. J. Berne, J. Chem. Phys. 83 (1985) 3172.
[14] J. E. Straub, M. Borkovec and B. J. Berne, J. Chem. Phys. 84 (1986) 1788.
[15] M. Topaler and N. Makri, J. Chem. Phys. 101 (1994) 7500 and References given therein.
[16] J.M. Sancho, A.H. Romero and K. Lindenberg, J. Chem. Phys. 109, 9888 (1998); K. Lindenberg, A.H. Romero and J.M. Sancho, Physica D 133, 348 (1999).
[17] M. Hillery, R. F. O’Connell, M. O. Scully and E. P. Wigner, Phys. Rep. 106 (1984) 121.
[18] D. Banerjee, B.C. Bag, S.K. Banik and D.S. Ray, Phys. Rev. E 65 (2002) 021109.
[19] S.K. Banik, B.C. Bag and D.S. Ray, Phys. Rev. E 65 (2002) 051106.
[20] D. Banerjee, S.K. Banik, B.C. Bag, and D.S. Ray, Phys. Rev. E 66 (2002) 051105.
[21] D. Banerjee, B.C. Bag, S.K. Banik and D.S. Ray, Physica A 318 (2003) 6.
[22] D. Barik, S.K. Banik and D.S. Ray, J. Chem. Phys. 119 (2003) 680.
[23] D. Barik, B. C. Bag and D.S. Ray, J. Chem. Phys. 119 (2003) 12973.
[24] D.J. Tannor and D. Kohen, J. Chem. Phys. 100 (1994) 4932.
[25] D. Kohen and D.J. Tannor, 103 (1995) 6013; D. Kohen and D. J. Tannor, Adv. Chem. Phys. 111 (1999) 219.
[26] P. G. Wolynes, Phys. Rev. Lett. 47 (1987) 968.
[27] B. Sundaram and P.W. Milonni, Phys. Rev. E 51 (1995) 1971.
[28] A.K. Pattanayak and W.C. Schieve, Phys. Rev. E 50 (1994) 3601.
[29] T. Kato and Y. Tanimura, J. Chem. Phys. 20 (2004) 260 and T. Kato and Y. Tanimura, J. Chem. Phys. 117 (2002) 6221.
[30] E. Pollak, J. Chem. Phys. 85 (1986) 865.
[31] E. Pollak, J. Chem. Phys. 88 (1988) 1959.
[32] E. Pollak, Phys. Rev. B 40 (1989) 2138.
[33] E. Pollak, Phys. Rev. A, 33 (1986) 4244.
[34] R.F. Grote and J.T. Hynes, J. Chem. Phys. 73 (1980) 2715.
[35] E. C. Titchmarsh, Introduction of the Theory of Fourier Integrals. (Oxford University Press, London, 1937).
[36] A. G. Sveshnikov and A. N. Tikhonov, The Theory of Functions of a Complex Variable (Mir Publishers, Moscow, 1973).
Figure Captions

Fig.1. A schematic plot of the potential defined in Eq.(6.1)

Fig.2. Quantum rate, $\Gamma/\Gamma_Q$, (where $\Gamma_Q = (\omega_0/2\pi)\chi \exp\left[-\frac{V^+}{\hbar\lambda_0(n_0(\lambda_0)+\frac{1}{2})}\right]$), in the non-Markovian regime is plotted against dissipation parameter, $\gamma$, for three different temperatures $k_B T = 0.0$ (solid line), $k_B T = 1.0$ (dashed line) and $k_B T = 5.0$ (dotted line) with $V^+ = 20.0$, $a = 0.03042$, $b = 0.5$ and $\tau_c = 1.333$.

Fig.3. Quantum turnover (solid line) is compared with classical turnover $R$ of Pollak, Grabert and Hänggi (dotted line) in the non-Markovian regime for two different temperatures $k_B T = 1.0$ and $k_B T = 2.0$, other parameters remain same as Fig.2.

Fig.4. The comparison of Kramers’ turnover for $V^+ = 26.188$, $a = 0.0266$, $b = 0.5$ at $kT = 1.788$. The solid line represents the quantum turnover by the present method, the dotted line represents the calculation by Rips and Pollak.[10]

Fig.5. The same as in Fig.4 but for $k_B T = 2.617$
Fig. 1
Fig. 2
Fig. 3

$\frac{\Gamma}{\Gamma_Q}$ vs $\gamma$

$kT = 1.0$

$kT = 2.0$
Fig. 4
Fig. 5