A generalization of Wolynes factor in activated processes

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Abstract

Kramers-Grote-Hynes factor is the key nonequilibrium contribution to rate constant of a reaction over and above the transition state theory rate in the spatial limited regime. Wolynes in eighties introduced a quantum correction to the overall rate coefficient. This is responsible for tunneling and quantum enhancement of rate at low temperature. However, its validity is restricted to activated tunneling region or above crossover temperature. Based on a quantum formulation of the normal mode analysis, we suggest a generalization of Wolynes factor and a consequent multidimensional transition state rate expression which are valid in the deep tunneling region down to zero degree Kelvin.
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. 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.

While Kramers’ theory is based on classical Markovian description, eighties saw a number of important generalization of Kramers theory in several directions by a number of groups. An important endeavor in this context is the inclusion of a quantum equilibrium factor, known as Wolynes factor, in the generalized Kramers’ or equivalently multidimensional transition state theory rate constant. This term allows tunneling as a possible decay route of the metastable state in addition to the usual thermally activated processes and is responsible for quantum enhancement of rate at low temperature. However, the validity of the Wolynes factor is restricted to the activated tunneling regime or above crossover temperature. Based on a positive definite Wigner function formalism within a normal mode description we generalize Wolynes factor and thereby multidimensional transition state rate expression which are valid in the deep tunneling region and vacuum limit.

The outlay of the paper is as follows. In the following Sec.II we discuss a quantum Langevin equation which allows us to realize a c-number Hamiltonian amenable to a 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. We work out the rate expression and the Wolynes factor in the appropriate limits. The paper is concluded in Sec.IV.
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:

$$\hat{H} = \frac{\hat{p}^2}{2} + V(\hat{q}) + \sum_{i=1}^{N} \left\{ \frac{\hat{p}_i^2}{2} + \frac{1}{2} \left( \omega_i \hat{x}_i - \frac{c_i}{\omega_i} \hat{\phi} \right)^2 \right\}$$ (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 $[\hat{x}_i, \hat{p}_j] = i\hbar \delta_{ij}$. Here masses have been assumed to be unity.

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

$$\hat{F}(t) = \sum_{j} \left[ \left\{ \frac{\omega_j^2}{c_j} \hat{x}_j(0) - \hat{\phi}(0) \right\} \frac{c_j^2}{\omega_j^2} \cos \omega_j t + \frac{c_j}{\omega_j} \hat{p}_j(0) \sin \omega_j t \right]$$ (2.3)

and

$$\gamma(t) = \sum_{j=1}^{N} \frac{c_j^2}{\omega_j^2} \cos \omega_j t$$ (2.4)

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)

$$\frac{1}{2} \{ \langle \hat{F}(t) \hat{F}(t') \rangle_{QS} + \langle \hat{F}(t') \hat{F}(t) \rangle_{QS} \} = \frac{1}{2} \sum_{j=1}^{N} \hbar \omega_j \left( \coth \frac{\hbar \omega_j}{2k_B T} \right) \frac{c_j^2}{\omega_j^2} \cos \omega_j (t - t')$$ (2.6)
where \( \langle \ldots \rangle_{QS} \) refers to quantum statistical average on bath degrees of freedom and is defined as

\[
\langle \hat{O} \rangle_{QS} = \frac{\text{Tr} \hat{O} \exp(-\hat{H}_{\text{bath}}/k_B T)}{\text{Tr} \exp(-\hat{H}_{\text{bath}}/k_B T)}
\] (2.7)

for any operator \( \hat{O}(\{\omega_i^2/c_j\hat{x}_j - \hat{q}_j\}, \{\hat{p}_j\}) \) where \( \hat{H}_{\text{bath}}(\sum_{i=1}^{N}[\hat{p}_i^2/2 + 1/2(\omega_i\hat{x}_i - \omega_i^2\hat{q}_i)^2]) \) at \( t = 0 \). By Trace we mean the usual quantum statistical average. Eq. (2.6) is the fluctuation-dissipation relation with the noise operators ordered appropriately in the quantum mechanical sense.

To construct a c-number Langevin equation\(^{20,21} \) we proceed from Eq. (2.2). We carry out a quantum mechanical average of Eq. (2.2)

\[
\langle \hat{q}(t) \rangle + \int_0^t dt' \gamma(t-t')\langle \hat{q}(t') \rangle + \langle V'(\hat{q}) \rangle = \langle \hat{F}(t) \rangle
\] (2.8)

where the quantum mechanical average \( \langle \ldots \rangle \) is taken over the initial product separable quantum states of the particle and the bath oscillators at \( t = 0 \), \( |\phi\rangle \{ |\alpha_1 \rangle |\alpha_2 \rangle \ldots |\alpha_N \rangle \} \). Here \( |\phi\rangle \) denotes any arbitrary initial state of the particle and \( |\alpha_i \rangle \) corresponds to the initial coherent state of the \( i \)-th bath oscillator. \( |\alpha_i \rangle \) is given by \( |\alpha_i \rangle = \exp(-|\alpha_i|^2/2) \sum_{n_i=0}^{\infty} (\alpha_i^{n_i} / \sqrt{n_i!}) |n_i \rangle \), \( \alpha_i \) being expressed in terms of the mean values of the shifted co-ordinate and momentum of the \( i \)-th oscillator, \( \{\omega_i^2/c_i\langle \hat{x}_i(0) \rangle - \langle \hat{q}(0) \rangle \} = (\sqrt{\hbar/2\omega_i})(\alpha_i + \alpha_i^\ast) \) and \( \langle \hat{p}_i(0) \rangle = i\sqrt{\hbar\omega_i/2}(\alpha_i - \alpha_i^\ast) \), respectively. It is important to note that \( \langle \hat{F}(t) \rangle \) of Eq. (2.8) is a classical-like noise term which, in general, is a non-zero number because of the quantum mechanical averaging and is given by \( \langle \hat{F}(t) \rangle \equiv f(t) \);

\[
f(t) = \sum_j \left[ \left\{ \frac{\omega_j^2}{c_j} \langle \hat{x}_j(0) \rangle - \langle \hat{q}(0) \rangle \right\} \frac{c_j^2}{\omega_j^2} \cos \omega_j t + \frac{c_j}{\omega_j} \langle \hat{p}_j(0) \rangle \sin \omega_j t \right]
\] (2.9)

It is convenient to rewrite the c-number equation (2.8) as follows;

\[
\langle \hat{q}(t) \rangle + \int_0^t dt' \gamma(t-t')\langle \hat{q}(t') \rangle + \langle V'(\hat{q}) \rangle = f(t)
\] (2.10)

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 \( \{\omega_j^2/c_j\langle \hat{x}_j(0) \rangle - \langle \hat{q}(0) \rangle \} \), \{\hat{p}_j\} \) of the bath oscillators are distributed according to a canonical distribution of Gaussian form as
\[ P_j = N \exp \left\{ -\frac{\langle \hat{p}_j(0) \rangle^2 + \frac{c_j^2}{\omega_j^2} \{\omega_j^2 \langle \hat{x}_j(0) \rangle - \langle \hat{q}(0) \rangle \}^2}{2\hbar \omega_j \left( \bar{n}_j(\omega_j) + \frac{1}{2} \right)} \right\} \]  

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

\[ \langle O_j \rangle_S = \int O_j \, P_j \, d\langle \hat{p}_j(0) \rangle \, d\{((\omega_j^2/c_j) \langle \hat{x}_j(0) \rangle - \langle \hat{q}(0) \rangle) \} \]  

Here \( \bar{n}_j \) indicates the average thermal photon number of the \( j \)-th oscillator at temperature \( T \) and \( \bar{n}_j(\omega_j) = 1/\exp (\hbar \omega_j/k_BT) - 1 \) and \( N \) is the normalization constant.

The distribution (2.11) and the definition of statistical average (2.12) imply that \( f(t) \) must satisfy

\[ \langle f(t) \rangle_S = 0 \]  

and

\[ \langle f(t)f(t') \rangle_S = \frac{1}{2} \sum_j \hbar \omega_j \left( \coth \frac{\hbar \omega_j}{2k_BT} \right) \frac{c_j^2}{\omega_j^2} \cos \omega_j(t - t') \]  

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.(2.6). It is important to emphasize that the ansatz (2.11) is a canonical Wigner distribution for a shifted harmonic oscillator\(^{18,19}\) and an exact solution of Wigner equation, 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.(2.6) 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.(2.10) to add the force term \( V'(\langle \hat{q} \rangle) \) on both sides of Eq.(2.10) and rearrange it to obtain\(^{20,21}\)

\[ \dot{q} = p \]  
\[ \dot{p} = -\int_0^t dt' \gamma(t - t') p(t') - V'(q) + f(t) + Q \]
where we put \( \langle \dot{q}(t) \rangle = q(t) \) and \( \langle \dot{p}(t) = p(t) \) for notational convenience and

\[
Q = V'(\langle \dot{q} \rangle) - \langle V'(\dot{q}) \rangle
\]  
(2.17)

represents the quantum correction due to the system degrees of freedom. Eq. (2.16) 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 (2.13) and (2.14) and a quantum fluctuation term \( Q^{20,21,22,23} \) characteristic of the non-linearity of the potential\(^{24}\).

Referring to the quantum nature of the system in the Heisenberg picture, we write\(^{22,23}\).

\[
\hat{q}(t) = q + \delta \hat{q}
\]
(2.18)
\[
\hat{p}(t) = p + \delta \hat{p}
\]
(2.19)

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 \( [\delta \hat{q}, \delta \hat{p}] = i\hbar \). Using Eqs. (2.18) and (2.19) in \( \langle V'(\hat{q}) \rangle \) and a Taylor series expansion around \( \langle \hat{q} \rangle \) it is possible to express \( Q \) as

\[
Q(q, \langle \delta \hat{q}^n \rangle) = -\sum_{n \geq 2} \frac{1}{n!} V^{(n+1)}(q) \langle \delta \hat{q}^n \rangle
\]  
(2.20)

Here \( V^{(n)}(q) \) is the n-th derivative of the potential \( V(q) \). For example, the second order \( Q \) is given by \( Q = -\frac{1}{2} V''(q) \langle \delta \hat{q}^2 \rangle \). The calculation of \( Q^{20,21,22,23} \) therefore rests on quantum correction terms, \( \langle \delta \hat{q}^n \rangle \) which are determined by solving the quantum correction equations as discussed in the following subsection.

A. Quantum correction equations

We now return to operator equation (2.2) and put (2.18) and (2.19) and use of Eq. (2.10) to obtain the following operator equations

\[
\dot{\delta \hat{q}} = \delta \hat{p}
\]  
(2.21)
\[
\dot{\delta p} + \int_0^t \gamma(t - t') \delta \dot{p}(t') \, dt' + V''(q) \delta \dot{q} + \sum_{n \geq 2} \frac{1}{n!} V^{(n+1)}(q) \left( \delta \dot{q}^n - \langle \delta \dot{q}^n \rangle \right) = \tilde{F}(t) - f(t)
\]  

(2.22)

Eqs.(2.21-2.22) form the key element for calculation of quantum mechanical correction due to nonlinearity of the system potential. Depending on nonlinearity of the potential and memory kernel we consider the following cases separately.

1. **Arbitrary memory kernel and harmonic potential**

We consider the friction kernel to be arbitrary but decaying and the potential as harmonic for which the derivatives of \( V(q) \) higher than second vanishes. After quantum mechanical averaging over the initial bath states \( \prod_{i=1}^{\infty} \{ |\alpha_i(0)\rangle \} \) only, the Eqs.(2.21-2.22) yield

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

(2.23)

\[
\dot{\delta q} = - \int_0^t \gamma(t - t') \delta \dot{p}(t') \, dt' - \omega^2 \delta \dot{q}
\]  

(2.24)

where \( \omega^2 = V''(q) \), a constant and \( \omega \) is the frequency of the harmonic oscillator. The above operator equation can be solved exactly by Laplace transform technique to obtain

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

(2.25)

where \( C_p(t) \) is obtained as the inverse Laplace transform of \( \widetilde{C}_p(s) \) given by

\[
\widetilde{C}_p(s) = \frac{1}{s^2 + s \, \widetilde{\gamma}(s) + \omega^2}
\]  

(2.26)

with \( \widetilde{\gamma}(s) \) as

\[
\widetilde{\gamma}(s) = \int_0^\infty \gamma(t) e^{-st} \, dt
\]  

(2.27)

is the Laplace transform of the friction kernel \( \gamma(t) \). After squaring and quantum mechanical averaging over arbitrary initial system state \( |\phi\rangle \), Eq.(2.25) yields
\[
\langle \delta \dot{q}^2(t) \rangle = \langle \delta \dot{q}^2(0) \rangle C_q^2(t) + \langle \delta \dot{p}^2(0) \rangle C_p^2(t) \\
+ C_p(t) C_q(t) \{ \langle \delta \dot{p}(0) \delta \dot{q}(0) \rangle + \langle \delta \dot{q}(0) \delta \dot{p}(0) \rangle \}
\]

with \( C_q(t) = 1 - \omega^2 \int_0^t C_p(t') dt' \).

2. **Exponential memory kernel and arbitrary potential**

This corresponds to a commonly occurring situation for which the bath modes are assumed to follow a Lorentzian distribution characterized by a density function \( \rho(\omega) \) such that for Eq.(2.4) in the continuum limit we write

\[
\frac{c^2(\omega)}{\omega^2} \rho(\omega) = \frac{2}{\pi} \frac{\Gamma}{1 + \omega^2 \tau_c^2}
\]

where \( \Gamma \) is the dissipation constant in the Markovian limit and \( \tau_c \) refers to correlation time. The memory kernel is exponential and \( \gamma(t) \) is given by

\[
\gamma(t) = \frac{\Gamma}{\tau_c} e^{-|t|/\tau_c}
\]

In this case the quantum correction equations (2.21) and (2.22) after quantum mechanical averaging over bath states may be rewritten

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

\[
\dot{\delta} \hat{p} = -V''(q) \delta \hat{q} - \sum_{n \geq 2} \frac{1}{n!} V^{(n+1)}(q) (\delta \hat{q}^n - \langle \delta \hat{q}^n \rangle) + \delta \hat{z}
\]

\[
\dot{\delta} \hat{z} = -\frac{\Gamma}{\tau_c} \delta \hat{p} - \frac{1}{\tau_c} \delta \hat{z}
\]

where we have introduced an auxiliary operator \( \delta \hat{z} \) to bypass the convolution integral in Eq.(2.22). Making use of the Eqs.(2.31,2.33) we derive the quantum correction equations up to second order to obtain

\[
\langle \delta \dot{q}^2 \rangle = \langle \delta \dot{q} \delta \hat{p} + \delta \hat{p} \delta \dot{q} \rangle
\]
\[ \langle \dot{\delta q} \delta p + \delta \dot{\delta q} \rangle = 2 \langle \delta p^2 \rangle - 2V''(q)\langle \delta q^2 \rangle + \langle \delta q \delta \dot{z} + \delta \dot{z} \delta q \rangle - V'''(q)\langle \delta q^3 \rangle \] (2.35)

\[ \langle \dot{\delta p}^2 \rangle = -V''(q)\langle \delta q \delta \dot{p} + \delta \dot{p} \delta q \rangle + \langle \delta \dot{p} \delta \dot{z} + \delta \dot{z} \delta \dot{p} \rangle - \frac{1}{2}V'''(q)\langle \delta q^2 \delta \dot{z} + \delta \dot{z} \delta q^2 \rangle \] (2.36)

\[ \langle \delta \dot{p} \delta \dot{z} + \delta \dot{z} \delta \dot{p} \rangle = -V''(q)\langle \delta q \delta \dot{z} + \delta \dot{z} \delta q \rangle - \frac{1}{2}V'''(q)\langle \delta q^2 \delta \dot{z} + \delta \dot{z} \delta q^2 \rangle \]

\[ - \frac{2\Gamma}{\tau_c} \langle \delta \dot{p}^2 \rangle - \frac{1}{\tau_c} \langle \delta \dot{p} \delta \dot{z} + \delta \dot{z} \delta \dot{p} \rangle + 2 \langle \delta \dot{z}^2 \rangle \] (2.37)

\[ \langle \delta q \delta \dot{z} + \delta \dot{z} \delta q \rangle = \langle \delta \dot{p} \delta \dot{z} + \delta \dot{z} \delta \dot{p} \rangle - \frac{\Gamma}{\tau_c} \langle \delta \dot{p} \delta \dot{p} + \delta \dot{p} \delta \dot{p} \rangle - \frac{1}{\tau_c} \langle \delta q \delta \dot{z} + \delta \dot{z} \delta q \rangle \] (2.38)

\[ \langle \delta \dot{z}^2 \rangle = -\frac{\Gamma}{\tau_c} \langle \delta \dot{p} \delta \dot{z} + \delta \dot{z} \delta \dot{p} \rangle - \frac{2}{\tau_c} \langle \delta \dot{z}^2 \rangle \] (2.39)

Discarding the third and higher order terms in Eqs. (2.34-2.39) we obtain a set of closed equations which can be solved numerically along with Eqs. (2.15) and (2.16), using suitable initial conditions for calculating the leading order (second order) contribution to quantum corrections in \( Q \). A standard choice of initial conditions corresponding to minimum uncertainty states is \( \langle \delta q^2(0) \rangle = \hbar/2\omega \), \( \langle \delta p^2(0) \rangle = \hbar \omega/2 \) and \( \langle \delta q(0)\delta \dot{p}(0) + \delta \dot{p}(0)\delta q(0) \rangle = \hbar \) with the other moments (Eqs. (2.37-2.39)) being set at zero. The procedure may be extended to include higher order quantum effects without difficulty and may be easily adopted for numerical simulation of quantum Brownian motion.

**B. Calculation of quantum statistical averages**

Summarizing the discussions of the last two sections \( A \) and \( B \) we now see that the Langevin dynamics in \( c \)-numbers can be calculated for a stochastic process by solving Eqs. (2.15) and (2.16) for quantum mechanical mean values simultaneously with quantum correction equations which describe quantum fluctuation around these mean values. In principle for nonlinear system the equations for quantum corrections constitute an infinite set of hierarchy which must be truncated after a desired order, in practice, to make the system of
equations closed. Care must be taken to distinguish among the three averages, the quantum mechanical mean \( \langle \hat{O} \rangle (= O) \), statistical average over quantum mechanical mean \( \langle O \rangle_s \) and the usual quantum statistical average \( \langle \hat{O} \rangle_{QS} \) as discussed in Sec.II. To illustrate the relation among them let us calculate, for example, the quantum statistical averages \( \langle \hat{q} \rangle_{QS} \), \( \langle \hat{q}^2 \rangle_{QS} \) and \( \langle \hat{q}^2 \hat{p} \rangle_{QS} \). By (2.18) and (2.19) we write

\[
\hat{q} = q + \delta \hat{q} \\
\langle \hat{q} \rangle_{QS} = \langle q + \delta \hat{q} \rangle_{QS} = \langle q \rangle_s + \langle \delta \hat{q} \rangle_s = \langle q \rangle_s
\]  

Again

\[
\langle \hat{q}^2 \rangle_{QS} = \langle (q + \delta \hat{q})^2 \rangle_{QS} = \langle q^2 \rangle_s + \langle \delta \hat{q}^2 \rangle_s
\]  

In the case of harmonic potential, \( \langle \delta \hat{q}^2 \rangle \) as given by (2.28) is independent of \( q \) or \( p \) so that one may simplify (2.42) further as

\[
\langle \hat{q}^2 \rangle_{QS} = \langle q^2 \rangle_s + \langle \delta \hat{q}^2 \rangle
\]  

In Ref.\(^{20}\) the explicit exact expressions for \( \langle \hat{q}^2 \rangle_{QS} \) and \( \langle \hat{p}^2 \rangle_{QS} \) have been derived for harmonic oscillator and they are found to be in exact agreement with those of Grabert et al.\(^{25}\). For anharmonic potential, however, one must have to use (2.42) to carry out further the statistical average over \( \langle \delta \hat{q}^2 \rangle \) i.e. \( \langle \langle \delta \hat{q}^2 \rangle_s \), since it is a function of stochastic variables \( q \) and \( p \) according to quantum correction equations. Furthermore we consider \( \langle \hat{q}^2 \hat{p} \rangle_{QS} \)

\[
\langle \hat{q}^2 \hat{p} \rangle_{QS} = \langle (q + \delta \hat{q})(p + \delta \hat{p}) \rangle_{QS} = \langle q^2 p \rangle_s + \langle p \delta \hat{q}^2 \rangle_s + \langle \delta \hat{q}^2 \delta \hat{p} \rangle_s + 2 \langle q \delta \hat{q} \delta \hat{p} \rangle_s
\]  

The essential element of the present approach is thus expressing the quantum statistical average as the sum of statistical averages of set of functions of quantum mechanical mean values and dispersions. Langevin dynamics being coupled to quantum correction equations,
the quantum mechanical mean values as well as the dispersions are computed simultaneously for each realization of the stochastic path. A statistical average implies the averaging over many such paths similar to what is done to calculate statistical averaging by solving classical Langevin equation. Before leaving this section we mention a few pertinent points.

First, the distinction between the ensemble averaging by the present procedure and by the standard approach using Wigner function is now clear. From Eq. (2.44) we note that, for example,

\[ \langle \hat{q}^2 \hat{p} \rangle_{QS} = \int q^2 p W(q,p) \neq \langle q^2 p \rangle_S \] (2.45)

where \( W(q,p) \) is the Wigner function for system operators. (This is not to be confused with the Wigner function we introduced in (2.11) for the bath oscillators.)

Second, our formulation of the Langevin equation coupled to quantum correction equations belongs to quantum stochastic process derived by c-number noise, which is classical-like in form. Its numerical solutions can be obtained in the same way as one proceeds in a classical theory.

Third, quantum nature of the dynamics appears in two different ways. The heat bath is quantum mechanical in character whose noise properties are expressed through quantum fluctuation-dissipation relation. The nonlinearity of the system potential, on the other hand, gives rise to quantum correction terms. Thus the classical Langevin equation can be easily recovered (i) in the limit \( \hbar \omega \ll k_B T \) to be applied in the Eq. (2.14) so that one obtains the classical fluctuation-dissipation relation and (ii) if the quantum dispersion term \( Q \) vanishes.

C. c-number Hamiltonian and normal mode description

The c-number Hamiltonian corresponding to Langevin equation (2.15) and (2.16) is given by

\[ H = \frac{p^2}{2} + \left[ V(q) + \sum_{n \geq 2} \frac{1}{n!} V^{(n)}(q) \langle \delta q^n \rangle \right] + \sum_{i=1}^{N} \left\{ \frac{p_{i}^2}{2} + \frac{1}{2} \left( \omega_i x_i - \frac{c_i}{\omega_i} q \right)^2 \right\} \] (2.46)

Note that the above Hamiltonian is different from our starting Hamiltonian operator (2.1) because of the c-number nature of (2.46). \( \{x_i, p_i\} \) are the quantum mean value of the co-ordinate and the momentum operators of the bath oscillators.
The spectral density function is defined as

\[
J(\omega) = \frac{\pi}{2} \sum_{i=1}^{N} \frac{c_i^2}{\omega_i} \delta(\omega - \omega_i)
\] (2.47)

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

\[
V(q) = V^\dagger - \frac{1}{2} \omega_b^2 q^2 + V_2(q)
\] (2.48)

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. (2.48) the quantum correction part in the Hamiltonian Eq. (2.46) becomes

\[
\sum_{n \geq 2} \frac{1}{n!} V^{(n)}(q) \langle \delta q^n \rangle = -\frac{\omega_b^2}{2} B_2 + V_3(q)
\] (2.49)

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 \( \langle \delta q^n \rangle \) to indicate its time average since it is sufficient to consider 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. Putting (2.48) and (2.49) in the Hamiltonian (2.46) we obtain

\[
H = H_0 + V_N(q)
\] (2.50)

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

\[
H_0 = \left[ \frac{p^2}{2} + \sum_i \frac{p_i^2}{2} \right] + \left[ V_1^\dagger - \frac{1}{2} \omega_b^2 q^2 + \sum_i \frac{1}{2} \left( \omega_i x_i - \frac{c_i}{\omega_i} q \right)^2 \right]
\] (2.51)

and

\[
V_N(q) = V_2(q) + V_3(q)
\] (2.52)

and

\[
V_1^\dagger = V^\dagger - \frac{B_2}{2} \omega_b^2
\]
$V_2(q)$ 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\textsuperscript{26}.

Following Pollak, we diagonalize the force constant matrix $T$ of the Hamiltonian (2.51) with the matrix $U$

$$UT = \lambda^2 U$$

where $U$ provides the transformation from old co-ordinates to the normal co-ordinates

$$
\begin{pmatrix}
\rho \\
y_1 \\
y_2 \\
\vdots \\
y_N
\end{pmatrix}
= U
\begin{pmatrix}
q \\
x_1 \\
x_2 \\
\vdots \\
x_N
\end{pmatrix}
$$

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

$$H_0 = \frac{1}{2} \dot{\rho}^2 + V_1 + \frac{1}{2} \lambda_b^2 \rho^2 + \sum_{i=1}^{N} \frac{1}{2} (y_i^2 + \lambda_i^2 y_i^2)$$

(2.55)

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:

$$\lambda_i^2 = -\omega_i^2 \left[ 1 + \sum_{j=1}^{N} \frac{\omega_j^2}{\omega_j^2 + \lambda_i^2} \right]^{-1}$$

(2.56)

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

(2.57)

where (2.56) and (2.57) correspond to normal mode frequencies of the unstable mode and the i-th bath oscillator respectively.

The transformation (2.54) implies
\[ q = u_{00} \rho + \sum_{j=1}^{N} u_{j0} y_j \]  

(2.58)

and it has been shown\textsuperscript{26} that \( u_{00} \) and \( u_{j0} \) may be expressed as

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

(2.59)

and

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

(2.60)

Making use of the spectral density function \textsuperscript{(2.47)} and Laplace transformation of \( \gamma(t) \), Eq.\textsuperscript{(2.50)} and Eq.\textsuperscript{(2.59)} may be written in the continuum limit as

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

(2.61)

and

\[ u_{00}^2 = \left[ 1 + \frac{2}{\pi} \int_{0}^{\infty} d\omega \frac{\omega J(\omega)}{\lambda_b^2 + \omega^2} \right]^{-1} \]  

(2.62)

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;

\[ \omega_b^2 \prod_{i=1}^{N} \omega_i^2 = \lambda_b^2 \prod_{i=1}^{N} \lambda_i^2 \]  

(2.63)

and

\[ \omega_0^2 \prod_{i=1}^{N} \omega_i^2 = \lambda_0^2 \prod_{i=1}^{N} \Lambda_i^2 \]  

(2.64)

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,
\[ H'_0 = \frac{1}{2} \rho'^2 + \frac{1}{2} \lambda^2_0 \rho'^2 + \left\{ \sum_{i=1}^{N} \frac{1}{2} \dot{y}'^2_i + \frac{1}{2} \Lambda^2_i y'^2_i \right\} \]  

(2.65)

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

\[
\begin{align*}
\lambda^2_0 &= \omega^2_0 \left[ 1 + \sum_{j=1}^{N} \frac{c_j^2}{\omega_j^2 (\omega_j^2 - \lambda^2_0)} \right]^{-1} \\
\Lambda^2_i &= \omega^2_0 \left[ 1 + \sum_{j=1}^{N} \frac{c_j^2}{\omega_j^2 (\omega_j^2 - \Lambda^2_j)} \right]^{-1}, \quad i = 1, 2...N
\end{align*}
\]

(2.66) \hspace{2cm} (2.67)

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 \( V(q) \). In the normal mode description of \( (N + 1) \) oscillators according to the Hamiltonian (2.55) 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\(^{18,19} \) of \( N \) uncoupled harmonic oscillators plus one inverted we have

\[
P_{eq} = z^{-1} \exp \left[ -\frac{1}{2} \rho'^2 + \frac{1}{2} \lambda^2_0 \rho'^2 \right] \prod_{i=1}^{N} \exp \left\{ -\frac{1}{2} \dot{y}'^2_i + \frac{1}{2} \Lambda^2_i \dot{y}'^2_i \right\}
\]

(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.(2.65). The corresponding distribution in the well is

\[
P_{eq} = z^{-1} \exp \left[ -\frac{1}{2} \rho'^2 + \frac{1}{2} \lambda^2_0 \rho'^2 \right] \prod_{i=1}^{N} \exp \left\{ -\frac{1}{2} \dot{y}'^2_i + \frac{1}{2} \Lambda^2_i \dot{y}'^2_i \right\}
\]

(3.2)

which can be normalized to obtain

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

(3.3)

The identity relation (2.64) can be used to transform to the following form
\[ z^{-1} = \frac{\omega_0}{2\pi h\lambda_0(n_0(\lambda_0) + \frac{1}{2})} \prod_{i=1}^{N} \frac{\omega_i}{2\pi h\lambda_i(n_i(\Lambda_i) + \frac{1}{2})} \]  

(3.4)

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

\[ P_{eq} = \frac{\omega_0}{2\pi h\lambda_0(n_0(\lambda_0) + \frac{1}{2})} \frac{\lambda_b}{\omega_b} \chi \exp \left[ -\frac{\frac{1}{2}\dot{\rho}^2 + V_1^\dagger - \frac{1}{2}\lambda^2_b \rho^2}{\hbar \lambda_0(n_0(\lambda_0) + \frac{1}{2})} \right] \]  

(3.5)

where

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

(3.6)

The total energy of the unstable mode is

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

(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 \( t, E \), respectively with unit Jacobian, the equilibrium distribution function (3.5) is given by,

\[ f_{eq}(E) = \frac{\omega_0}{2\pi h\lambda_0(n_0(\lambda_0) + \frac{1}{2})} \frac{\lambda_b}{\omega_b} \chi \exp \left[ -\frac{E}{\hbar \lambda_0(n_0(\lambda_0) + \frac{1}{2})} \right] \]  

(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

\[ \Gamma = \int_{V_1^\dagger}^{\infty} f(E) \, dE \]  

(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
\[ \Gamma_{QMTST} = \frac{\omega_0}{2\pi} \frac{\lambda_b}{\omega_b} \chi \exp \left[ -\frac{V^\dagger}{\hbar \lambda_0 (\pi_0(\lambda_0) + \frac{1}{2})} \right] \]  

(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, it contains two important factors. First, an exponential Arrhenius term where the usual thermal factor \( k_B T \) is replaced by \( \hbar \lambda_0 (\pi_0(\lambda_0) + \frac{1}{2}) \) 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 oscillator 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 and the quantum rate valid above cross-over temperature can easily be recovered from \( \chi \) in the appropriate limit.

B. Derivation of Wolynes factor from \( \chi \) and limiting rate expression at low temperature above cross-over

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

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

(3.11)

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

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

(3.12)

Therefore \( \chi \) reduces to \( \Xi \) (say) the Wolynes factor.
$$\Xi = \prod_{i=1}^{N} \frac{\lambda_i \left( \sinh \frac{\hbar \lambda_i}{2k_B T} \right)^{-1}}{\Lambda_i \left( \sinh \frac{\hbar \Lambda_i}{2k_B T} \right)^{-1}}$$

From identities (2.63) and (2.64) it follows

$$\prod_{i=1}^{N} \lambda_i = \omega_b \prod_{i=1}^{N} \omega_i$$
$$\prod_{i=1}^{N} \Lambda_i = \omega_0 \prod_{i=1}^{N} \omega_i$$

respectively, and we have

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

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

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

Furthermore \((\lambda_0 \omega_b)/(\omega_0 \lambda_b)\) can be rewritten as \(\frac{\omega_b}{\omega_0} \frac{(h \lambda_0/k_B T)}{(h \lambda_0/k_B T)}\) which may be approximated in the form \((\omega_b/\omega_0) \sinh(h\lambda_0/2k_B T)/\sinh(h\lambda_0/2k_B T)\). Eq. (3.17) then reduces to

$$\Xi = \frac{\omega_b}{\omega_0} \frac{\sinh(h\lambda_0/2k_B T)}{\sinh(h\lambda_0/2k_B T)} \prod_{i=1}^{N} \frac{\sinh(h\Lambda_i/2k_B T)}{\sinh(h\lambda_i/2k_B T)}$$

This is the well known Wolynes expression derived in 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. The quantity \(\Xi\) approaches unity when the temperature far exceeds the cross-over temperature. The Wolynes factor may be approximated to yield a form at low temperature (valid above cross-over temperature) as \(\exp \left[ \frac{h^2}{24} \frac{(\omega_0^2 + \omega_b^2)}{(k_B T)^2} \right]\). This term is responsible for well known \(T^2\) enhancement of rate due to quantum effects. With this form of \(\Xi\) and \(\exp \left[ -\frac{V^*}{\hbar \lambda_b (\tau_0(\lambda_b)+\frac{1}{2})} \right]\) reducing to \(\exp \left[ -\frac{V^*}{k_B T} \right]\) above the cross-over regime we obtain from (3.10) the rate expression derived earlier.
\[
\Gamma = \frac{\omega_0}{2\pi} \frac{\lambda_b}{\omega_b} \exp \left[ \frac{\hbar^2}{24} \left( \omega_b^2 + \omega_0^2 \right) \right] \exp \left[ -\frac{V^4}{k_B T} \right] \quad (3.19)
\]

Our general expression (3.10) valid in the deep tunneling regime, \textit{i.e.}, down to vacuum regime.

IV. 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 noise correlation and temperature down to vacuum limit. The following pertinent points are noteworthy.

(i) We have shown that the expression for quantum rate coefficient is a product of four terms, \textit{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 \textit{i.e.} the generalized Arrhenius term. 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 multidimensional 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 classical limit of the quantum rate expression depends on Wigner, generalized Wolynes factor. It is easy to see that they reduce to Arrhenius factor, unity respectively in the limit \( \hbar \omega \ll k_B T \).

(iii) The present theory 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.

The quantum theory as presented here is based on a canonical quantization procedure and a description of equilibrium by positive definite Wigner’s thermal distribution for the bath rather than path integral or master equation formalism. The approach has been used
and are in use in many related issues. The systematic improvement can be made by taking care of the quantum corrections of higher orders.

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