doi: 10.31674/book.2025ccbsse012

Non-Adiabatic Escape Rate of a Quantum Dissipative System from a Rapidly Oscillating Periodic Potential

Anindita Shit

Department of Chemistry, Kandi Raj College, Kandi, Murshidabad 742137, West Bengal, India

Corresponding Author's E-mail: anindita.pchem@gmail.com

Abstract

Escape rate under the influence of a high-frequency field has appeared as a theme of topical interest in different variants of the kinetic model of chemical and biological phenomena over more than two decades. The escape rate of a quantum system modulated by a rapid, time-periodic external force is studied here in the presence of environmental dissipation with the effect of the foundational process of the intricate interplay of the temperature, field and the system parameters on the escape rate profile with the help of the modified Langevin equation obtained by systematically expanding in terms of (1/ω) via perturbative methods using the Kapitza−Landau time scale and quantum gauge transformation in the frame of the Floquet theorem. Present formalism, which is classical in appearance yet quantum in nature, provides the full time-independent activated escape rate that often plays a pivotal role in different processes and phenomena ranging from diffusion in condensed phases to biological and chemical reactions. This work, therefore, furnishes avenues of controlling such escape rates in realistic systems of arbitrary complexity and generality.

Keywords: *Effective Potential; Langevin Equation; Multiple Scale Perturbation Analysis; Path Integral Formalism; Quantum Dissipative Systems*

Introduction

In the field of physical, biological and chemical sciences, the system-reservoir model is a broadly acknowledged concept which is capable of explaining a plethora of phenomena. Thus, comprehending this model is inherently significant. The analysis of such systems becomes difficult due to the perturbation that varies over time. Usually when the system is driven by slow external perturbation, it remains in equilibrium with the potential with no time lag, but the situation becomes tricky when the external disturbance becomes periodic with higher field frequencies. A comprehensive methodology has not been established in existing studies to get insights into such dynamics (Jung 1993, Reichl & Kim 1996, Jülicher, Ajdari & Prost 1997, Doering & Gadoua 1992, Gammaitoni *et al.*, 1998, Reimann, Grifoni & Hänggi 1997, Reimann 2002). Thus, the investigation of responses of a system to rapid periodic external forces is crucial in the field of chemical dynamics in condensed matter. The dynamics of the non-equilibrium system are complex and varied, as substantial deviations from the Boltzmann distribution can arise, giving rise to effects that may appear partially counterintuitive. Generally, when a particle is exposed to an external time-dependent drive, its escape rate from a metastable state is also found to be time- dependent. Thus, one of the main challenges lies in determining the escape rate. Studying escape rate offers a

deeper understanding of the system's overall dynamics as in an escape process where the system moves over its metastable state.

Literature Review

The most fundamental theory for studying such dynamical processes is the theory of the Brownian motion. The classical theory of Brownian motion which involves either Langevin equation (Coffey *et al*., 2004) or Fokker−Planck equation (Risken 1989) is well-recognised but analysis for similar quantum systems are still absent as quantum dissipation involves a more intricate formulation compared to classical dissipation (Gammaitoni *et al.*, 1998, Coffey *et al*., 2004, Coffey, Kalmykov & Waldron, 2004, Luchinsky, McClintock & Dykman, 1998, Weiss 2012, Hänggi, Talkner & Borkovec, 1990, Hänggi & Jung, 1995, Grabert, Schramm & Ingold, 1988, Hänggi & Ingold, 2005, Tanimura & Ishizaki, 2009, Coffey, Garanin & McCarthy, 2001, Coffey *et al.*, 2013) Recently, the quantum mechanics of systems driven by rapid external perturbations has gained attention where the driving force becomes nonadiabatic. In the regime of high-frequency external perturbations, the notion of eigenstate transitions for the unperturbed Hamiltonian ceases to be applicable. Several methodologies have been proposed to incorporate quantum effects in a diffusion equation (Machura *et al.*, 2004, Łuczka, Rudnicki & Hänggi, 2005, Ford & O'Connell, 2006, Tsekov, 1995, Tsekov 2007, Ankerhold, Pechukas & Grabert, 2001, Coffey *et al.*, 2007a, Banerjee *et al.*, 2002, Banerjee *et al.*, 2004, Ghosh, Barik & Ray, 2007, Bhattacharya, Chattopadhyay & Ray Chaudhuri, 2009, Ghosh *et al.*, 2010, Bhattacharya *et al.*, 2009, Dillenschneider & Lutz, 2009). The Wigner formulation is a valuable method for calculating quantum corrections to classical dissipation models(Leggett & Caldeira, 1983, Tanimura & Wolynes, 1991,Tanimura & Wolynes, 1992, Tanimura, 2006, and Tanaka & Tanimura, 2009, Tanaka & Tanimura, 2010, Sakurai & Tanimura, 2011, Tanimura, 2012, Coffey *et al.*,2007a, Coffey *et al.*, 2007b, Coffey, Kalmykov & Titov, 2007, García-Palacios & Zueco, 2004, García-Palacios, 2004). The Wigner space formulation of the hierarchy equations of motion has been shown to offer a useful approach for exploring diverse phenomena in several significant areas (Tanimura & Wolynes, 1991; Tanimura & Wolynes; 1992, Tanimura, 2006; Tanaka & Tanimura, 2009; Tanaka & Tanimura, 2010; Sakurai & Tanimura, 2011; Tanimura, 2012). Among the various approaches to modelling dissipation, the path integral formulation of quantum mechanics stands out for its effectiveness (Grabert, Schramm & Ingold, 1987; Grabert, Schramm & Ingold, 1988; Ingold, 1997; Ingold, 2002). Ankerhold, Pechukas and Grabert (2001) proposed a quantum extension of the Smoluchowski equation, originating from the precise path-integral method to reduced dynamics. This formulation offers structural flexibility to include higher-order quantum corrections in the original quantum Smoluchowski equation and has been implemented to a broad range of problems, encompassing the systems both with and without external perturbation (Ankerhold, 2004; Machura *et al*., 2006; Maier & Ankerhold, 2010). The chapter addresses the study of escape rates from a metastable potential well in the high-frequency modulation regime, where the frequency of modulation surpasses all other relevant system frequencies. Here multiple scale perturbation theory (MSPT) (Shit, Chattopadhyay & Ray Chaudhury, 2013; Orszag & Bender, 1978) is used in the framework of the traditional path integral approach in order to handle non-Markovian and nonsecular quantum system-bath interplay. Path integral formulation is often used to study

decay from a metastable state of a quantum system modulated by rapid periodic oscillation. Periodic modulation is easier to understand conceptually regardless of the range of the frequency variation. However, as the system is no longer in thermal equilibrium, calculation of the escape rate is more complex. This work seeks to explore the underlying mechanisms of internal noise (resulting from SB coupling) and external driving, and to understand their mutual interaction. The outcomes of this work may prove useful in the context of modelling cold atom control through electromagnetic field interactions. In recent years, Shit *et al* have proposed a perturbative framework for examining the classical and quantum motion of particles influenced by high-frequency fields, particularly when the nature of the driving force shifts to nonadiabatic (Shit, Chattopadhyay & Ray Chaudhuri, 2011; Shit, Chattopadhyay & Chaudhuri, 2012). In this chapter, it has been shown that, on timescales longer than the perturbation period, the (Langevin) dynamics can be represented by replacing the periodic perturbation with an effective potential which does not have any explicit time dependence. Successful applications to different physical problems showcase the effectiveness of this method. Although there are results (Lehmann, Reimann & Hänggi, 2000; Kim *et al.*, 2010) that are precise when noise strength tends to zero, at elevated frequencies, the method fails to perform under fixed noise strength conditions. This regime is addressed in this chapter. It is crucial to recognise that many phenomena critically depend on activated escape, including diffusive processes in the solid-state materials and on their surfaces, as well as various chemical reactions. Consequently, finding methods to control escape rates is essential.

Discussion

The dynamics of quantum particles are studied here, which are acted upon by a fast-oscillating periodic force using the Kapitza time window (that involves separating the system's variables into slow and fast components). This development facilitates solving the problem in the presence of friction and random forces. Let us begin with considering a system-reservoir Hamiltonian in the proposal by Zwanzig (2001), where the reservoir is represented by a collection of harmonic oscillators characterised by frequencies, masses and the system is subjected to a high-frequency periodic field. The model can be expressed by the following Hamiltonian:

$$\begin{aligned}\hat{H} &= \hat{H}_S(\hat{x},\hat{p}) + \hat{H}_B\left(\{\hat{q}_j\},\{\hat{p}_j\}\right) + \hat{H}_{SB}\left(\hat{x},\{\hat{q}_j\}\right) \\ &= \frac{\hat{p}^2}{2m} + \hat{V}_0(\hat{x}) + \hat{V}_1(\hat{x},\omega t) + \sum_{j=1}^{N}\left\{\frac{\hat{p}_j^2}{2m_j} + \frac{1}{2}m_j\omega_j^2\left(\hat{q}_j - \frac{c_j\hat{x}}{m_j\omega_j^2}\right)^2\right\} \end{aligned} \quad (1)$$

Here, $\hat{x}$ and $\hat{p}$ represent the position and momentum operators of the system, while $\left(\{\hat{q}_j\},\{\hat{p}_j\}\right)$ denote the sets of position and momentum operators for the bath oscillators. The confining potential is given by $\hat{V}_0(\hat{x})$ that the system would execute alone without any external drive, and $\hat{V}_1$ represents the potential due to the external driving with period T whose time average over one period is zero:

$$\hat{V}_1(\hat{x},\omega(t+\tau)) = \hat{V}_1(\hat{x},\omega t) \quad (2)$$

and

$$\frac{1}{T}\int_0^T dt\, \hat{V}_1(\hat{x}, \omega t) = 0$$

Following the customary approach of excluding the bath variables yields the quantum Langevin equation as

$$m\dot{\hat{x}} + \int_0^t dt'\gamma(t-t')\dot{\hat{x}}(t') + \frac{\partial \hat{V}(\hat{x},\omega t)}{\partial \hat{x}} = \hat{\xi}(t) \quad (3)$$

where $\hat{V} = \hat{V}_0 + \hat{V}_1$ (4)

and the damping kernel $\gamma(t-t') = \frac{1}{\pi}\int_{-\infty}^{+\infty} d\,\omega[J(\omega)/\omega]\cos\omega\,(t-t')$ (5)

The fluctuation operator, $\hat{\xi}(t)$ follows the fluctuation-dissipation relation. The bath's dual effects—fluctuation and dissipation—collaborate to uphold the system's thermal equilibrium in accordance with the fluctuation-dissipation theorem.

$$\langle\hat{\xi}(t)\hat{\xi}(t') + \hat{\xi}(t')\hat{\xi}(t)\rangle = \hbar\int_{-\infty}^{+\infty}\frac{d\omega}{\pi}J(\omega)\coth\left(\frac{\hbar\boldsymbol{\omega}}{2k_BT}\right)\cos\omega(t-t') \quad (6)$$

Here the initial configuration of the bath degrees of freedom is used to compute the average. The friction coefficient γ clearly depicts that energy is irreversibly lost from the system to the environment. Here the Ohmic regime (i.e., strict Markovian limit) is considered with the spectral distribution function J(ω) J(ω) = mγω which characterises the bath dynamics. In this context, γ reflects the correlation time of the bath-induced noise by characterising the spectral distribution width of the bath modes. It is to be mentioned here that the solutions of Eq. (3) are very complicated due to the involvement of time-dependent potential. It can typically be obtained numerically using various approximate methods. However, when the frequency of driving force is large and very large compared with all the other relevant system frequencies, a solution may be attainable, contingent on the type of problem being analysed. The force $\hat{F}(x,\omega t)$, due to the external time periodic field is given by:

$$\hat{F}(x,\omega t) = -\hat{V}_1'(x,\omega t) \text{ with } \omega \gg \frac{1}{T} \quad (7)$$

Here the oscillation of the particle induced by the external time periodic force is considered to be very small so that the particle lacks sufficient time to respond before the periodic force switches direction i.e., the acceleration over one period is barely affected by the periodic force. As a result, it is beneficial to separate the motion of the particle into "slow" and "fast" components. The Hamiltonian in Eq. (1) is time periodic, i.e., [Ĥ (t + T) = Ĥ(t)]. Thus, the dynamical analysis of such systems can be possible by using Floquet theorem which enables the simplification of the periodic or quasiperiodic time-dependent Schrödinger equation into a system of time-independent coupled equations or a Floquet matrix eigenvalue problem (Grifoni & Hänggi, 1998). The Schrödinger equation is as follows:

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi \quad (8)$$

The following Floquet states linked to their corresponding quasi-energies ε can be used to express solutions to Equation (8) as a linear combination:

$$\psi_\varepsilon = \left(\exp -\frac{i}{\hbar}\varepsilon t\right) \mathbb{U}_\varepsilon(x, \omega t) \tag{9}$$

$\mathbb{U}_\varepsilon(x, \omega t)$ denotes eigenstates of the Floquet Hamiltonian: $\hat{H}_F = -i\hbar\left(\frac{\partial}{\partial t}\right) + \hat{H}$. This reflects the key idea of the Bloch–Floquet theorem applied to time-dependent systems. Here, $\mathbb{U}_\varepsilon(x, \omega(t+T)) = \mathbb{U}_\varepsilon(x, \omega t)$ with ω = (2π/T). Floquet state has a "slow" part, $\left(\exp -\frac{i}{\hbar}\varepsilon t\right)$ (with the choice $0 \leq \varepsilon/\hbar \leq \omega$), which provides details regarding the quasienergies, and a "fast" part, $\mathbb{U}_\varepsilon(x, \omega t)$ that is solely dependent on the fast time τ = ωt. Thus, one can derive an equation of motion for the slow dynamics that encodes the system's quasienergies, with the necessary steps detailed as follows. Initially, a unitary gauge transformation $\exp(i\hat{T}(t))$, is aimed to be performed where $\hat{T}(t)$ is a Hermitian operator is periodic in time [$\hat{T}(t+T) = \hat{T}(t)$] with the same period as the Hamiltonian $\hat{H}$. This transformation removes the explicit time-dependence from the Hamiltonian making it time-independent in the new gauge. The transformed time independent Hamiltonian helps in deriving the equation of motion for the "slow" component. Eq. (8), expressed in the new gauge with $\chi = \exp(i\hat{T}(t))\psi$, is now written as

$$i\hbar\frac{\partial\chi}{\partial t} = \hat{H}_{eff}\chi \tag{10}$$

According to Floquet theory, χ has the same periodic behaviour as the Hamiltonian operator Ĥ and the Hermitian operator T̂. In the transformed gauge, χ represents a Floquet state characterised by the quasienergy ε. So, one may express the effective time-independent Hamiltonian as

$$\hat{H}_{eff} = \exp(i\hat{T}(t))\hat{H}\exp\left(-i\hat{T}(t)\right) + i\hbar\left[\frac{\partial\exp(i\hat{T}(t))}{\partial t}\right]\exp(-i\hat{T}(t)) \tag{11}$$

The gauge transformation of Eq. (11) can be expressed in terms of fast time τ

$$\hat{H}_{eff} = \exp(i\hat{T})\hat{H}\exp\left(-i\hat{T}\right) + i\hbar\omega\left[\frac{\partial\exp(i\hat{T})}{\partial\tau}\right]\exp(-i\hat{T}) \tag{12}$$

In the subsequent analysis, $\hat{T}$ is treated as a perturbative term of order ω^{-1} in the high-frequency limit. Therefore, $\hat{H}_{eff}$ and $\hat{T}$ are expanded in powers of 1/ω as

$$\hat{H}_{eff} = \sum_{n=0}^{\infty}\frac{1}{\omega^n}\hat{H}_n^e \tag{13}$$

$$\hat{T} = \sum_{n=0}^{\infty}\frac{1}{\omega^n}\hat{T}_n \tag{14}$$

The choice of $\hat{T}$ ensures that $\hat{H}_{eff}$ remains independent of time, order by order. Thus, $\hat{H}_j^e$ is expressed in terms of $\hat{T}_1$, $\hat{T}_2$, …,$\hat{T}_{j+1}$, after which $\hat{T}_{j+1}$ is selected such that $\hat{H}_j^e$ is rendered time independent. Using the operator expressions to compute the terms in Eq. (11), one can get

$$\exp(i\hat{T})\hat{H}\exp\left(-i\hat{T}\right) = \hat{H} + i\left[\hat{T},\hat{H}\right] - \frac{1}{2!}\left[\hat{T},\left[\hat{T},\hat{H}\right]\right] - \frac{1}{3!}\left[\hat{T},\left[\hat{T},\left[\hat{T},\hat{H}\right]\right]\right] + \cdots \tag{15}$$

and

$$\frac{\partial \exp(i\hat{T})}{\partial \tau}\exp\left(-i\hat{T}\right) = i\frac{\partial \hat{T}}{\partial \tau} - \frac{1}{2!}\left[\hat{T}, \frac{\partial \hat{T}}{\partial \tau}\right] - \frac{1}{3!}\left[\hat{T}\left[\hat{T}, \frac{\partial \hat{T}}{\partial \tau}\right]\right] + \cdots \quad (16)$$

In the leading term, $O(\omega^0)$, $\hat{H}_0^e$ is described by

$$\hat{H}_0^e = \frac{\hat{p}^2}{2m} + \hat{V}_0(\hat{x}) + \hat{H}_{\boldsymbol{B}} + \hat{H}_{\boldsymbol{SB}} + \hat{V}_1(\hat{x}, \tau) - \hbar\frac{\partial \hat{T}_1}{\partial \tau} \quad (17)$$

$\hat{V}_0$, $\hat{V}_1$, $\hat{H}_B$, and $\hat{H}_{SB}$ do not depend on $\hat{p}$ at all. For canceling the time dependence of $\hat{H}_0^e$, we choose

$$\hat{T}_1 = \frac{1}{\hbar}\int_0^\tau d\tau'\, \hat{V}_1(\hat{x}, \tau') \quad (18)$$

The integration constant is chosen as zero to get rid of the secular terms. Now, the substitution of Eq. (18) into Eq. (17) gives the leading order of the effective Hamiltonian

$$\hat{H}_0^e = \frac{\hat{p}^2}{2m} + \hat{V}_0(\hat{x}) + \hat{H}_{\boldsymbol{B}} + \hat{H}_{\boldsymbol{SB}} \quad (19)$$

Using Eq. (12) the effective Hamiltonian can be expressed in the order ω^{-1}as

$$\hat{H}_1^e = i\left[\hat{T}_1, \hat{H}\right] - \hbar\frac{\partial \hat{T}_2}{\partial \tau} - \frac{i\hbar}{2}\left[\hat{T}_1, \frac{\partial \hat{T}_1}{\partial \tau}\right] \quad (20)$$

As evident from Eq. (18), Since $\hat{T}_1$ is exclusively dependent on x̂, so it will commute with its time derivative as well as with $\hat{V}_0$, $\hat{H}_B$, and $\hat{H}_{SB}$. Thus, $\hat{H}_1^e = i\left[\hat{T}_1, (\hat{p}^2/2m)\right] - \hbar\left(\partial \hat{T}_2/\partial \tau\right)$. It is always possible to select $\hat{T}_2$ to be periodic such that $\left(\partial \hat{T}_2/\partial \tau\right) = i/\hbar\left[\hat{T}_1, (\hat{p}^2/2m)\right]$, leading to the vanishing of $\hat{H}_1^e$. Subsequently, $\hat{T}_2$ is determined using Equation (18) and the coordinate representation of the momentum operator p̂

$$\hat{T}_2 = \frac{i}{2m}\int_0^\tau \partial\tau \int_0^\tau \partial\tau \hat{V}_1^{"}(\hat{x}, \tau) + \frac{i}{m}\int_0^\tau \partial\tau \int_0^\tau \partial\tau \hat{V}_1'(\hat{x}, \tau)\frac{\partial}{\partial x} \quad (21)$$

With this choice, $\hat{H}_1^e$ becomes zero. At the next order, ω^{-2}, $\hat{H}_2^e$ can be calculated from

$$\hat{H}_2^e = i\left[\hat{T}_2, \hat{H}\right] - \frac{1}{2}\left[\hat{T}_1, \left[\hat{T}_1, \hat{H}\right]\right] - \hbar\frac{\partial \hat{T}_3}{\partial \tau} - \frac{i\hbar}{2}\left[\hat{T}_1, \frac{\partial \hat{T}_2}{\partial \tau}\right] - \frac{i\hbar}{2}\left[\hat{T}_2, \frac{\partial \hat{T}_1}{\partial \tau}\right] + \frac{\hbar}{6}\left[\hat{T}_1, \left[\hat{T}_1, \frac{\partial \hat{T}_1}{\partial \tau}\right]\right] \quad (22)$$

Using $\hat{H} = \hat{H}_0^e + \hbar\left(\partial \hat{T}_1/\partial \tau\right)$ and $\left(\partial \hat{T}_2/\partial \tau\right) = \left[\hat{T}_1, (\hat{p}^2/2m)\right] = \left[\hat{T}_1, \hat{H}\right]$, one obtains

$$\hat{H}_2^e = i\left[\hat{T}_2, \hat{H}_0^e\right] - \hbar\frac{\partial \hat{T}_3}{\partial \tau} + \frac{i\hbar}{2}\left[\hat{T}_2, \frac{\partial \hat{T}_1}{\partial \tau}\right] \quad (23)$$

Next, a periodic $\hat{T}_3$ is selected to counterbalance the time dependency of $\hat{H}_2^e$. It is found that $\hat{H}_2^e$ contains a time-independent component given by $i\hbar/2\left[\hat{T}_2, \left(\partial \hat{T}_1/\partial \tau\right)\right]$. To ensure the periodicity of $\hat{T}_2$, $\hat{T}_3$ is chosen so that

$$\frac{\partial \hat{T}_3}{\partial \tau} = \frac{i}{\hbar}\left[\hat{T}_2, \hat{H}_0^e\right] + \frac{i}{2}\left[\hat{T}_2, \frac{\partial \hat{T}_1}{\partial \tau}\right] - \frac{i}{2}\overline{\left[\hat{T}_2, \frac{\partial \hat{T}_1}{\partial \tau}\right]} \quad (24)$$

The overbar expresses the time average over one period. From Eqs. (18) and (21), $\hat{T}_3$ is found to be

$$\hat{T}_3 = -\frac{\hbar}{m^2}\int_0^\tau \partial\tau \int_0^\tau \partial\tau \int_0^\tau \partial\tau \hat{V}_1''(\hat{x},\tau)\frac{\partial^2}{\partial x^2} - \frac{\hbar}{m^2}\int_0^\tau \partial\tau \int_0^\tau \partial\tau \int_0^\tau \partial\tau \hat{V}_1'''(\hat{x},\tau)\frac{\partial}{\partial x} - \frac{\hbar}{4m^2}\int_0^\tau \partial\tau \int_0^\tau \partial\tau \int_0^\tau \partial\tau \hat{V}_1^4(\hat{x},\tau) - \frac{1}{m\hbar}\hat{V}_0'(\hat{x})\int_0^\tau \partial\tau \int_0^\tau \partial\tau \int_0^\tau \partial\tau \hat{V}_1'(\hat{x},\tau) + \frac{1}{2m\hbar}\int_0^\tau \partial\tau\ \hat{Q}(\hat{x},\tau) + \hat{I}(\hat{x},\hat{p}) \quad (25)$$

where

$$\hat{Q}(\hat{x},\tau) = im\hbar\left[\hat{T}_2, \frac{\partial\hat{T}_1}{\partial\tau}\right] - im\hbar\overline{\left[\hat{T}_2, \frac{\partial\hat{T}_1}{\partial\tau}\right]} = \overline{\hat{V}_1'(\hat{x},\tau)\int_0^\tau \partial\tau \int_0^\tau \partial\tau \hat{V}_1'(\hat{x},\tau)} - \hat{V}_1'(\hat{x},\tau)\int_0^\tau \partial\tau \int_0^\tau \partial\tau \hat{V}_1'(\hat{x},\tau) \quad (26)$$

and $\hat{I}(\hat{x},\hat{p})$ is the integration constant that is a Hermitian operator of $\hat{x}$ and $\hat{p}$ only. The determination of higher-order corrections necessitates understanding $\hat{I}$. Therefore, $\hat{I}$ does not need to be evaluated in the leading-order correction. Substituting Equation (25) into Equation (23) yields time-independent $\hat{H}_2^e$:

$$\hat{H}_2^e = \frac{i\hbar}{2}\overline{\left[\hat{T}_2, \frac{\partial\hat{T}_1}{\partial\tau}\right]} = \frac{1}{2m}\overline{\left[\int_0^\tau \partial\tau \hat{V}_1'(\hat{x},\tau)\right]^2} \quad (27)$$

The resulting time-independent effective Hamiltonian, which includes the non-zero leading-order contribution:

$$\hat{H}_{eff} = \frac{\hat{p}^2}{2m} + \hat{V}_{eff} + \hat{H}_{\boldsymbol{B}} + \hat{H}_{\boldsymbol{SB}} \quad (28)$$

Here the effective time-independent potential, which depends on the driving frequency and amplitude influencing the slow motion, is expressed as follows

$$\hat{V}_{eff} = \hat{V}_0(\hat{x}) + \frac{1}{2m\omega^2}\overline{\left[\int_0^\tau \partial\tau \hat{V}_1'(\hat{x},\tau)\right]^2} \quad (29)$$

Using the time-independent effective potential $\hat{V}_{eff}$, one can apply the established methodologies developed for such problems to address the original time-dependent issues. Thus, in the high-frequency regime, the slower dynamics are guided by the time-independent effective potential, which remains unaltered even in the presence of noise originating from the bath. The effective Hamiltonian can be interpreted as a quantum mechanical extension of the classical results by Kapitza (1986) and Landau and Lifshitz (1976), within the context of the SB model. Now the reduced Langevin equation expressing the slow variable becomes:

$$m\ddot{\hat{x}} + \int_0^t dt'\,\gamma(t-t')\dot{\hat{x}}(t') + \hat{V}_{eff}' = \xi(t) \quad (30)$$

Since Eq. (30) does not have explicit time dependence, its solution does not oscillate at the external frequency ω. The dynamics are governed by the nature of the effective potential (Fig. 1). Equations 29 and 30 stem from high-frequency perturbation theory, providing A method to convert a time-dependent problem into a time-independent framework approximately. This approach can be helpful in creating simplified models for condensed phase reactions.

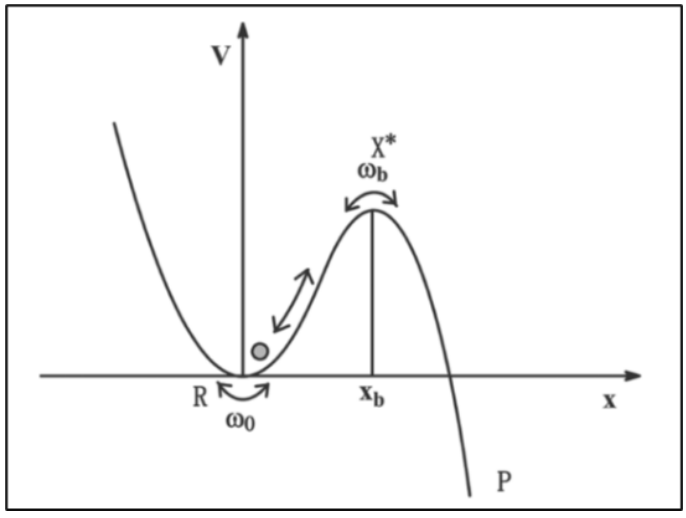

Figure 1: Graphical Representation of a Cubic Potential Where R Represents the Reactant State and P Denotes the Product State While X* Implies the Transition State (Shit, Chattopadhyay & Ray Chaudhuri, 2013)

To comprehend how the outcome from equation 30 may be applied to the stochastic dynamics of a system with periodic perturbations, it is helpful to analyse with a model. Consider a particle subject to an oscillating field ($V_0 = 0$),

$$V_1(x, \omega t) = Ae^{-\beta x^2} \sin(kx) \cos(\omega t + \phi) \tag{31}$$

Because the time-averaged potential energy cancels out, the influence of the oscillating field remains significant, even at elevated frequencies. As stated in equation 29, the slower component of the particle's motion can be roughly described as motion within an effective potential, which is governed by the ratio of the amplitude to the frequency of the external modulation.

$$V_{eff}(X) = \frac{A^2}{4m\omega^2} e^{-2\beta X^2} \omega [k \cos(kX) - 2\beta X \sin(kX)]^2 \tag{32}$$

$V_{eff}(X)$ is found to exhibit several local minima, two of these are more prominent in the parameters under consideration. Consequently, it can be concluded that a particle traversing such potential is likely to reside in one of these minima after an adequately extended period. As a result of dissipation, these minima are surrounded by basins of attraction. Therefore, when the friction dominates, the particle may become localised in one of the minima. Here the effective Hamiltonian does not have momentum-dependent couplings to the leading order (ω^{-2}) due to the very high frequency regime considered. This perspective makes quantum escape rate calculation easy and much less expensive. As per the earlier demonstration, some features of the time-dependent system may be captured by studying a suitable time-independent system governed by the Langevin equation (equation 30). It is now worth investigating whether both qualitative and quantitative results for the dissipation-driven escape from a metastable state can be obtained using a path-integral formulation

related to the Brownian motion (Ingold, 1997; Ingold, 2002) of quantum systems. In order to do so, a model system potential (say, a cubic potential, shown in Figure 1) is chosen so that an energy barrier of defined height separates the reactant and product states. Particles are initially confined in the well of state R by a large potential hump at X*. They quickly reach thermal equilibrium within the well. However, due to the perturbation, a small number of particles may gain sufficient energy to overcome the barrier and enter region P, where return is not possible. The particle undergoes stochastic motion inside the well until a substantial perturbation drives it to overcome the potential barrier.

$$V_0 = \frac{A}{2}x^2 - \frac{B}{3}x^3 \tag{33}$$

A and B are positive constants. The position coordinate x has its values at $x = 0$ implying the reactant state and $x = x_b$ marking transition states. The finite potential barrier separating the transition state and the reactant state by is expressed as $(A^3/6B^2)$. Here, the system and environment's remaining degrees of freedom act as a heat bath at temperature T. Eq. (33) can be rewritten for examining the escape from a metastable state as

$$V_0(x) = \frac{1}{2}\omega^2 x^2\left(1 - \frac{x}{x_0}\right) \tag{34}$$

A minima is located at $x = 0$ with with oscillations around this point having a frequency of ω_0 . A barrier appears at $x = (2/3)x_0$ with a potential barrier $V_b = (2/27)\omega_0^2 x_0^2$. Assuming harmonic behaviour is close to the barrier leads to:

$$V(x) = V_b - \frac{1}{2}\omega_b^2 x^2 \tag{35}$$

ω_b is the angular barrier frequency and V_b is the height of the potential barrier respectively located at x_b with $\omega_0 = \omega_b$. When the metastable state decays at a temperature T which is much higher than the crossover temperature, $T_0\ [= (\hbar\omega_R/2\pi k_B)]$ where thermal activation becomes dominant, and accounting for memory effects, the dissipation of the metastable state leads to the following quantum escape rate:

$$k^Q = f_{cl}\omega c_{qm}\exp\left(\frac{V_b}{K_B T}\right) \tag{36}$$

Hence, the barrier crossing is boosted by quantum modifications due to the introduction of a further quantum "channel" when the temperature is in the quantum-classical crossover region. This increase is due to two key quantum occurrences: the mean energy in the well is raised by quantum fluctuations, and when the particle is subjected to thermal excitation near the top of the potential barrier, these fluctuations promote tunnelling through the residual small barrier.

These two effects reduce the barrier height. In the present model, when $T \gg T_0$, f_{cl} becomes the attempt frequency or classical pre-exponential factor and is calculated as

$$\omega_R f_{cl} = \frac{\omega_0\omega_R}{2\pi\omega_b} \tag{37}$$

The frequency ω_R is a dissipation-renormalised quantity, determined by the largest positive solution of the equation: $\omega_R^2 + \omega_R\hat{\gamma}(\omega_R) = \omega_b^2$ and it corresponds to the well-known Kramers–Grote–Hynes frequency (Grote & Hynes, 1980; Hanggi & Mojtabai, 1982) described in the theory of non-Markovian rate processes. Renormalising the barrier frequency captures the influence of memory friction on the rate. Intriguingly, the renormalised frequency is the same as the one used to define the crossover temperature T_0. The quantum correction factor c_{qm} has no dimension and it describes how quantum effects enhance the classical rate. It can lead to a significant rate enhancement, even at temperatures considerably above T_0. As T approaches T_0 from above, the quantum correction factor exhibits a singularity. Using the standard functional integral approach (Grabert & Weiss, 1984), quantum mechanical correction factor can be expressed as:

$$c_{qm} = \prod_{n=1}^{\infty} \frac{\nu_n^2+\omega_0^2+\nu_n\hat{\gamma}(\nu_n)}{\nu_n^2-\omega_b^2+\nu\hat{\gamma}(\nu_n)} \tag{38}$$

Here $\hat{\gamma}(Z)$ is the Laplace transform of the damping kernel γ(z) where ν_n's are the Matsubara frequencies [2πkBT/$\hbar$]. As the temperature approaches T_0, i.e., the crossover temperature, c_{qm} approaches 1 and diverges exactly at T_0. In the classical limit, where $T = T_0$ [i.e., $T/T_0 \rightarrow \infty$] the rate expression under intermediate-to-high damping conditions yields the correct classical result:

$$k_{IHD}^{cl} = \left(\frac{\omega_0\omega_R}{2\pi\omega_b}\right)\exp\left(\frac{V_b}{k_BT}\right) \tag{39}$$

To extract leading quantum correction terms at elevated temperatures, Eq. (38) is reformulated as an exponential of a sum over logarithms, with each logarithm expanded in a power series of $k_BT/\hbar$.

$$c_{qm} = \exp\left[\frac{\hbar^2}{4\pi^2}\left(\omega_0^2+\omega_b^2\right)\sum_{n=1}^{\infty}\frac{1}{n^2}\right] = \exp\left[\frac{\hbar^2}{4\pi^2}\left(\frac{\omega_0^2+\omega_b^2}{(k_BT)^2}\right)\right] \tag{40}$$

Eq. 36, denoting the escape rate, may therefore be written as

$$k_{IHD}^{Q} = \left(\frac{\omega_0}{2\pi\omega_B}\right)\left(\sqrt{\frac{\gamma^2}{4}+\omega_b^2}-\frac{\gamma}{2}\right)\times\exp\left[\frac{\hbar^2}{4\pi^2}\left(\frac{\omega_0^2+\omega_b^2}{(K_BT)^2}\right)\right]\exp\left(\frac{V_b}{K_BT}\right) \tag{41}$$

This expression is valid in The Kramers regime, i.e., moderate to strong damping regime and for $T > T_0$ where the primary mechanism for escape is not quantum tunnelling, yet it contributes notable quantum corrections to the classical activation rate. At strong friction $\gamma \gg \omega_0$, ω_b with $T \gg T_0$, the quantum correction can be given by

$$c_{qm} = \exp\left[\frac{\hbar\left(\omega_0^2+\omega_b^2\right)}{2\pi k_BT}\left\{\Psi\left(1+\frac{\hbar\gamma}{2\pi k_BT}\right)-\Psi(1)\right\}\right] \tag{42}$$

where $\Psi(z)$ expresses digamma function. This simplified form, Eq. (42), is accurate only for systems with frequency-independent damping. The effective potential caused by external modulation is

$$V_{eff} = \frac{\tilde{A}}{2}x^2 - \frac{\tilde{B}}{3}x^3 \tag{44}$$

where

$$\tilde{A} = A + \frac{a^2}{2\omega^2} \tag{45}$$

It is clearly evident that the tuning of system parameters and the activation barrier height is influenced by external drive. Thus, the amplitude-to-frequency ratio of the driving modulation (a/ω) plays a crucial influence in determining the escape rate as well as the barrier height. The well and barrier are positioned at at $x_0 = 0$ and $x_b = \tilde{A}/B$, respectively and leading to an effective potential barrier:

$$V_b^{eff} = \frac{\tilde{A}^3}{6B^2} \tag{46}$$

In the intermediate-to-high damping regime, where the energy dissipated per cycle far exceeds thermal energy, and assuming unit mass, the quantum Kramers rate for a rapid, periodically modulated particle can be expressed at times t > 1/ω, when the dynamics effectively become time-independent, as:

$$k_{IHD}^{Q} = \left(\frac{\widetilde{\omega}_0}{2\pi\widetilde{\omega}_b}\right)\left(\sqrt{\frac{\gamma^2}{4} + \widetilde{\omega}_b^2} - \frac{\gamma}{2}\right) \times \exp\left[\frac{\hbar^2}{4\pi^2}\left(\frac{\widetilde{\omega}_0^2 + \widetilde{\omega}_b^2}{(K_B T)^2}\right)\right] \exp\left(-\frac{V_b^{eff}}{K_B T}\right) \tag{47}$$

The classical counterpart of the rate can be written as:

$$k_{IHD}^{Cl} = \left(\frac{\widetilde{\omega}_0}{2\pi\widetilde{\omega}_b}\right)\left(\sqrt{\frac{\gamma^2}{4} + \widetilde{\omega}_b^2} - \frac{\gamma}{2}\right) \exp\left(-\frac{V_b^{eff}}{K_B T}\right) \tag{48}$$

Here $\widetilde{\omega}_0$ and $\widetilde{\omega}_b$ are the frequency terms involved with the time-independent effective potential at the well and at the top of the barrier, respectively. Equation 47 contains both the exponents and the prefactors modified by the applied external field. When external perturbation is absent, this result agrees well with the well-known Kramers model. This is a clear indication of the accuracy of this model. Obtaining this result through path-integral techniques is a complex and challenging task. This analysis demonstrates the interplay between the fixed-temperature Intermediate-to-high-damping quantum Kramers rate and the semi-classical approach within the multiple-scale perturbation theory framework for Brownian motion in rapidly varying periodic potential. While the calculation of the rate of escape in a rapidly driven quantum system from a static metastable state might seem overwhelmingly dependent on time and far from adiabatic, this work offers a perspective through which the dynamics can be understood in terms of a time-independent modified potential. Theoretical calculation of the dissipation-induced escape rate from a metastable state subjected to a fast-oscillating external field reveals two main effects on the escape rate, arising from the high-frequency nature of the field relative to the particle's dynamics. First, environmental disturbances alter the kinetics near the energy barrier's peak, thereby influencing the stationary flux across it. Second, the equilibrium statistical distribution in the source well transitions to a steady-state form, incorporating the influence of energy injected by the external driving force. Taking into account these pronounced dynamic changes, a

generalised form of escape rate can be developed which reveals how external perturbation affects the rate. Equation (47) is subsequently rewritten as a function of a/ω:

$$k_{IHD}^{Q} = \underbrace{\frac{1}{2\pi}\left(\sqrt{\frac{\gamma^2}{4}+\left(A+\frac{a^2}{2\omega^2}\right)}-\frac{\gamma}{2}\right)}_{I} \times \underbrace{\exp\left[\frac{\hbar^2}{12}\left\{\frac{A+\frac{a^2}{2\omega^2}}{(K_BT)^2}\right\}\right]}_{II} \times \underbrace{\exp\left[-\frac{\left(A+\frac{a^2}{2\omega^2}\right)^3}{6B^2K_BT}\right]}_{III} \tag{49}$$

Term II is found to be absent in k_{IHD}^{Cl} . The effect of temperature and the parameter ratio a/ω on the escape dynamics can be examined by considering cubic potential and studying how $\ln k$ varies with $1/T$ for a Brownian particle in it, capturing both external field influences and quantum effects (as discussed elaborately in Ref. (Shit, Chattopadhyay & Ray Chaudhuri, 2013). This analysis provides that in the low-temperature regime, dissipative quantum decay leads to a rise in the decay rate with temperature rise. The quantum correction effectively decreases the potential barrier, which increases the escape rate. The classical cases follow a linear trend, consistent with the Arrhenius law. However, at low temperatures (high 1/T), the plot becomes nonlinear due to quantum effects, specifically the term II in equation 49, which is a key observation of this study. The quantum term is modulated by temperature as T^{-2}, contributing to the deviation from linearity. This highlights the quantum nature of the system. The escape process involves two processes—one is thermal activation which becomes dominant at elevated temperatures, and the other one is quantum tunnelling which plays a key role as the temperature decreases. Decay at extremely low temperatures arises purely from quantum mechanisms. As the temperature increases, the system displays linear trends, reflecting more classical behaviour. Since thermal energy remains well below the barrier height, external driving becomes essential for activation. When there is no external perturbation, the traditional Kramers plot is obtained. Observations reveal that periodic, space-dependent, high-frequency perturbations significantly increase the classical transition rate of Brownian particles relative to the unperturbed case.

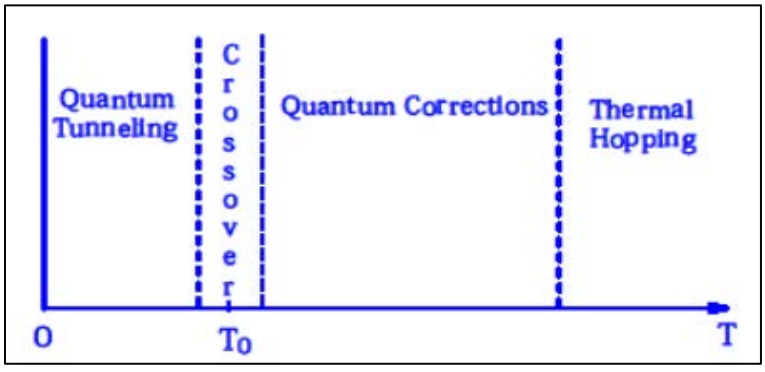

Figure 2: A Diagrammatic Representation Outlining the Temperature-Dependent Escape Dynamics Showing the Crossover Temperature T_0, Below Which Quantum Tunnelling Dominates Over Thermal Escape (Shit, Chattopadhyay & Ray Chaudhuri, 2013)

The expression in Eq. (44) reveals that with an increase in the ratio a/ω, the barrier height increases, which in turn decreases the escape rate. This behaviour is demonstrated through the plots depicting analytical quantum (Eq. 47) and classical (Eq. 48) nonadiabatic escape rates, as functions of a/ω at different temperatures (Shit, Chattopadhyay & Ray Chaudhuri, 2013). Additionally, it is observed that tunnelling contributes to an increased escape rate through an effective decrease in barrier height. The findings suggest that with a rising a/ω ratio, the role of external driving overtakes that of quantum tunnelling. An increase in the ratio a/ω results in a higher barrier results a notable reduction in the stimulated escape rate causing the Brownian particle to take a longer time to transition into the more stable well. Thus, it is also noteworthy that tuning the ratio of the external drive's amplitude to its frequency allows control over the system's lifetime in a metastable state, either extending or reducing it. As temperature rises, the classical rate gets enhanced as expected, but the quantum escape rate behaves differently. For significantly elevated a/ω ratios, the quantum escapes rate rises with temperature, while in the low a/ω range, higher thermal energy paradoxically reduces the quantum escape rate. This counterintuitive finding reveals an unexpected mechanism for enhancing system stability under nonequilibrium conditions, in stark contrast to classical system behaviour. The subtle coupling between the driving field and the intrinsic system parameters causes this unusual temperature effect, offering valuable insights into dynamics away from thermal equilibrium. The physical basis for this unforeseen outcome can be explained using equation 49. It has been observed that term III controls the effect of temperature on k_{IHD}^{Cl} and the classical escape rate gets enhanced with the elevation of temperature. But this is not the case for k_{IHD}^{Q} which includes two exponential components involving temperature, each with a different sign. The exponential components in equation 49 show that term II (stemming from field modulation) varies with T^{-1}, while term III (a pure quantum effect) shows a variation with T^{-2}. This asymmetric temperature dependence leads to the notable impact of temperature on k_{IHD}^{Q} as field parameters change. This analysis also illustrates how external perturbation influences the threshold or crossover temperature T_0, which marks the transition between quantum tunnelling and thermal activation. The current theoretical framework is applicable for temperatures above this crossover point. As shown in Figure 2, a clear transition occurs at T_0, where the dominant escape mechanism shifts from thermally activated hopping to quantum tunnelling. Since the dissipation mechanism dictates the magnitude of T_0, the comparative extents of the quantum and classical regimes vary with dissipation strength. For $T < T_0$, escape is primarily governed by quantum tunnelling. Under high-temperature conditions ($T \gg T_0$), the decay is predominantly due to thermal activation induced barrier escape, with negligible quantum contributions. However, in the vicinity of the crossover temperature (i.e., just above T_0), quantum fluctuations start to significantly affect the escape rate, enhancing it beyond classical predictions. This quantum contribution becomes increasingly prominent as the temperature decreases. Within the framework of the present model, the revised crossover temperature $\tilde{T}_0$ may be expressed as:

$$\tilde{T}_0 = \frac{\hbar}{2\pi k_B T}\left[\sqrt{\left(\omega_0^2 + \frac{\gamma^2}{4}\right)} - \frac{\gamma}{2}\right] \tag{50}$$

As a result, it is clear that $\tilde{T}_0$ depends on the modulation parameters in addition to the dissipation mechanism. From the form of the crossover temperature expression, it is evident that as a result of external driving, the modified crossover temperature exceeds that of the unmodulated system. Therefore, a remarkable aspect of this work is the extension of the temperature range in which quantum effects become significant. Specifically, as spatial friction increases, the crossover temperature, marking the shift from quantum tunnelling to thermal activation, also rises and it makes the quantum effects relevant at higher temperatures.

Conclusion

Barrier-crossing processes are fundamental to a wide array of physical, chemical, and biological systems. Despite extensive studies and various strategies developed to control activation under external perturbations, the field remains active, with many open questions yet to be addressed. Periodically modulated systems, which are far from thermal equilibrium, form an important class of such systems. The present study is to analyse the escape dynamics of a quantum Brownian system in contact with an Ohmic bath, driven by a high-frequency periodic monochromatic driving field—conditions that create a far-from-equilibrium environment that presents theoretical challenges. Using the path-integral approach within the "Kapitza-Landau time window" framework for the interactions between the system and the environment, under high-frequency modulation, the quantum system's behaviour is well approximated by a static effective Hamiltonian or potential. As a consequence, the barrier height becomes renormalised, and the escape rate acquires a nontrivial prefactor that intricately depends on the system and external field characteristics. Therefore, the field alters the activation energy for escape. This formulation delivers a time-independent rate expression that holds for intermediate-to-high damping, for temperatures exceeding the crossover temperature, and in the high-frequency driving regime where ω surpasses all other related system frequencies. The structure of the time-independent modified potential-shaped by amplitude-to-frequency ratio $\boldsymbol{a/\omega}$ plays a key role in determining the escape rate. Modifications arising from the applied perturbation and quantum mechanical contributions are also crucial in shaping the barrier-crossing dynamics. For a well-chosen set of field parameters, even a simplified static potential surface may see a substantial reduction in the net escape rate as the temperature increases. Therefore, the "extra dose" of external modulation does not always result in an increase in the rate of escape, which is a rare and paradoxical outcome. This stems from the subtle balance between dissipative forces and the applied modulation. While classical escape rates, such as those predicted by the Kramers model, generally rise with temperature under modulation, quantum escape rates display a much more nuanced and nontrivial temperature dependence. This study offers important understanding of how quantum mechanical effects modify reaction dynamics in condensed phases, especially in systems operating beyond equilibrium conditions.

Acknowledgement

The author expresses her gratitude to Professor Sudip Kumar Chattopadhyay and Professor Jyotipratim Ray Chaudhuri. She is thankful to Kandi Raj College, Kandi, Murshidabad, West Bengal, India.

References

Ankerhold, J. (2004). Overdamped quantum phase diffusion and charging effectsin Josephson junctions. *Europhysics Letters*, *67*(2), 280. https://doi.org/10.1209/epl/i2004-10067-y

Ankerhold, J., Pechukas, P., & Grabert, H. (2001). Strong friction limit in quantum mechanics: The quantum Smoluchowski equation. *Physical Review Letters, 87*, 086802 (1–4); Erratum: 2008, *101*, 119903. https://doi.org/10.1103/PhysRevLett.87.086802

Banerjee, D., Bag, B. C., Banik, S. K., & Ray, D. S. (2002). Approach to quantum Kramers' equation and barrier crossing dynamics. *Physical Review E, 65*, 021109 (1–13). https://doi.org/10.1103/PhysRevE.65.021109

Banerjee, D., Bag, B. C., Banik, S. K., & Ray, D. S. (2004). Solution of quantum Langevin equation: Approximations, theoretical and numerical aspects. *Journal of Chemical Physics, 120*, 8960–8972. https://doi.org/10.1063/1.1711593

Bhattacharya, S., Chattopadhyay, S., & Ray Chaudhuri, J. (2009). Investigation of noise-induced escape rate: A quantum mechanical approach. *Journal of Statistical Physics, 136*, 733–750. https://doi.org/10.1007/s10955-009-9802-5

Bhattacharya, S., Chaudhury, P., Chattopadhyay, S., & Ray Chaudhuri, J. (2009). Quantum transport in a periodic symmetric potential of a driven quantum system. *Physical Review E, 80*, 041127(1–14). https://doi.org/10.1103/PhysRevE.80.041127

Coffey, W. T., Garanin, D. A., & McCarthy, D. J. (2001). Crossover formulas in the Kramers theory of thermally activated escape rates—Application to spin systems. *Advances in Chemical Physics, 117*, 483–765. https://doi.org/10.1002/9780470141779.ch5

Coffey, W. T., Kalmykov, Y. P., & Titov, S. V. (2007). Solution of the master equation for Wigner's quasiprobability distribution in phase space for the Brownian motion of a particle in a double well potential. *Journal of Chemical Physics, 127*, 074502(1–10). https://doi.org/10.1063/1.2759486

Coffey, W. T., Kalmykov, Y. P., & Waldron, J. T. (2004). *The Langevin Equation* (2nd ed.). World Scientific: Singapore. https://doi.org/10.1142/5343

Coffey, W. T., Kalmykov, Y. P., Titov, S. V., & Mulligan, B. P. (2007). Quantum master equation in phase space: Application to the Brownian motion in a periodic potential. *Europhysics Letters, 77*, 20011(1–6). https://doi.org/10.1209/0295-5075/77/20011

Coffey, W. T., Kalmykov, Y. P., Titov, S. V., & Mulligan, B. P. (2007). Semiclassical master equation in Wigner's phase space applied to Brownian motion in a periodic potential. *Physical Review E, 75*, 041117. https://doi.org/10.1103/PhysRevE.75.041117

Coffey, W. T., Kalmykov, Y. P., Titovac, S. V., & Dowling, W. J. (2013). Longest relaxation time of relaxation processes for classical and quantum Brownian motion in a potential: Escape rate

theory approach. *Advances in Chemical Physics, 153*, 111–309. https://doi.org/10.1002/9781118571767.ch3

Coffey, W. T., Kalmykov, Y. P., Titovac, S. V., & Mulligan, B. P. (2007). Wigner function approach to the quantum Brownian motion of a particle in a potential. *Physical Chemistry Chemical Physics, 9*, 3361–3382. https://doi.org/10.1039/b614554j

Dillenschneider, R., & Lutz, E. (2009). Quantum Smoluchowski equation for driven systems. *Physical Review E, 80*, 042101(1–4). https://doi.org/10.1103/PhysRevE.80.042101

Doering, C. R., & Gadoua, J. C. (1992). Resonant activation over a fluctuating barrier. *Physical Review Letters*, *69*, 2318–2321. https://doi.org/10.1103/PhysRevLett.69.2318

Ford, G. W., & O'Connell, R. F. (2006). Anomalous diffusion in quantum Brownian motion with colored noise. *Physical Review A, 73*, 032103 (1–6). https://doi.org/10.1103/PhysRevA.73.032103

Gammaitoni, L., Hänggi, P., Jung, P., & Marchesoni, F. (1998). Stochastic resonance. *Reviews of Modern Physics*, *70*, 223–287. https://doi.org/10.1103/RevModPhys.70.223

García-Palacios, J. L. (2004). Solving quantum master equations in phase space by continued-fraction methods. *Europhysics Letters, 65*, 735–741. https://doi.org/10.1209/epl/i2003-10134-y

García-Palacios, J. L., & Zueco, D. (2004). The Caldeira–Leggett quantum master equation in Wigner phase space: Continued-fraction solution and application to Brownian motion in periodic potentials. *Journal of Physics A, 37*, 10735–10770. https://doi.org/10.1088/0305-4470/37/45/003

Ghosh, P. K., Barik, D., & Ray, D. S. (2007). Inhomogeneous quantum diffusion and decay of a meta-stable state. *Physics Letters A, 361*, 201–211. https://doi.org/10.1016/j.physleta.2006.08.090

Ghosh, P., Shit, A., Chattopadhyay, S., & Ray Chaudhuri, J. (2010). Escape of a driven particle from a metastable state: A semiclassical approach. *Journal of Chemical Physics, 132*, 244506(1–13). https://doi.org/10.1063/1.3443774

Grabert, H., & Weiss, U. (1984). Crossover from thermal hopping to quantum tunneling. *Physical Review Letters, 53*, 1787–1790. https://doi.org/10.1103/PhysRevLett.53.1787

Grabert, H., Schramm, P., & Ingold, G.-L. (1987). Localization and anomalous diffusion of a damped quantum particle. *Physical Review Letters, 58*, 1285–1288. https://doi.org/10.1103/PhysRevLett.58.1285

Grabert, H., Schramm, P., & Ingold, G.-L. (1988). Quantum Brownian motion: The functional integral approach. *Physics Reports, 168*, 115–207. https://doi.org/10.1016/0370-1573(88)90023-3

Grifoni, M., & Hänggi, P. (1998). Driven quantum tunneling. *Physics Reports, 304*, 229–354. https://doi.org/10.1016/S0370-1573(98)00022-2

Grote, R. F., & Hynes, J. T. (1980). The stable states picture of chemical reactions. II. Rate constants for condensed and gas phase reaction models. *Journal of Chemical Physics, 73*, 2715–2732. https://doi.org/10.1063/1.440485

Hänggi, P., & Ingold, G. L. (2005). Fundamental aspects of quantum Brownian motion. *Chaos, 15*, 026105 (1–12). https://doi.org/10.1063/1.1853631

Hänggi, P., & Jung, P. (1995). Colored noise in dynamical systems. *Advances in Chemical Physics*, *89*, 239–326. https://doi.org/10.1002/9780470141489.ch4

Hänggi, P., & Mojtabai, F. (1982). Thermally activated escape rate in presence of long-time memory. *Physical Review A, 26*, 1168–1170. https://doi.org/10.1103/PhysRevA.26.1168

Hänggi, P., Talkner, P., & Borkovec, M. (1990). Reaction-rate theory: Fifty years after Kramers. *Reviews of Modern Physics*, *62*, 251–341. And references therein. https://doi.org/10.1103/RevModPhys.62.251

Ingold, G.-L. (1997). In Quantum fluctuations. In S. Reynaud, E. Giacobino, & J. Zinn-Justin (Eds.), *Quantum Fluctuations* (pp. 577–584). Elsevier: New York. https://pubs.acs.org/doi/abs/10.1021/jp402565y

Ingold, G.-L. (2002). In Path integrals and their application to dissipative quantum systems. In A. Buchleitner & K. Hornberger (Eds.), *Lecture Notes in Physics* (Vol. 611, pp. 1–53). Springer: New York. https://doi.org/10.1007/3-540-45855-7_1

Jülicher, F., Ajdari, A., & Prost, J. (1997). Modeling molecular motors. *Reviews of Modern Physics*, *69*, 1269–1282. https://doi.org/10.1103/RevModPhys.69.1269

Jung, P. (1993). Periodically driven stochastic systems. *Physics Reports*, *234*, 175–295. https://doi.org/10.1016/0370-1573(93)90022-6

Kapitza, P. L. (1986). *Collected Papers of P. L. Kapitza* (Vol. 3, D. ter Haar, Ed.). Pergamon: New York.

Kim, C., Talkner, P., Lee, E. K., & Hänggi, P. (2010). Rate description of Fokker-Planck processes with time-periodic parameters. *Chemical Physics, 370*, 277–289. https://doi.org/10.1016/j.chemphys.2009.10.027

Landau, L. D., & Lifshitz, E. M. (1976). *Mechanics*. 3rd Edition. Pergamon: Oxford. Retrieved from: https://cimec.org.ar/foswiki/pub/Main/Cimec/MecanicaRacional/84178116-Vol-1-Landau-Lifshitz-Mechanics-3Rd-Edition-197P.pdf , Accessed on 21st December 2024.

Leggett, A. J., & Caldeira, A. O. (1983). Statistical thermodynamics of fluid hydrogen at high energy density. *Physica A, 121*, 587–596. https://doi.org/10.1016/0378-4371(85)90047-0

Lehmann, J., Reimann, P., & Hänggi, P. (2000). Surmounting oscillating barriers. *Physical Review Letters, 84*, 1639–1642. https://doi.org/10.1103/PhysRevLett.84.1639

Luchinsky, D. G., McClintock, P. V. E., & Dykman, M. I. (1998). Analogue studies of nonlinear systems. *Reports on Progress in Physics*, *61*, 889–997. 10.1088/0034-4885/61/8/001

Łuczka, J., Rudnicki, R., & Hänggi, P. (2005). The diffusion in the quantum Smoluchowski equation. *Physica A: Statistical Mechanics and its Applications, 351*, 60–68. https://doi.org/10.1016/j.physa.2004.12.007

Machura, L., Kostur, M., Hänggi, P., Talkner, P., & Łuczka, J. (2004). Consistent description of quantum Brownian motors operating at strong friction. *Physical Review E, 70*, 031107 (1–5). https://doi.org/10.1103/PhysRevE.70.031107

Machura, L., Kostur, M., Talkner, P., Łuczka, J., & Hänggi, P. (2006). Quantum diffusion in biased washboard potentials: Strong friction limit. *Physical Review E, 73*, 031105(1–7). https://doi.org/10.1103/PhysRevE.73.031105

Maier, S. A., & Ankerhold, J. (2010). Quantum Smoluchowski equation: A systematic study. *Physical Review E, 81*, 021107(1–14). https://doi.org/10.1103/PhysRevE.81.021107

Orszag, S., & Bender, C. M. (1978). *Advanced Mathematical Methods for Scientists and Engineers* (pp. xiv+-593). New York, NY, USA: McGraw-Hill.

Reduced hierarchy equations of motion approach to molecular vibrations. *Journal of Physical Chemistry A, 115*, 4009–4022. https://doi.org/10.1021/jp1095618

Reichl, L. E., & Kim, S. (1996). Stochastic chaos and resonance in a bistable stochastic system. *Physical Review E*, *53*, 3088–3095. https://doi.org/10.1103/PhysRevE.53.3088

Reimann, P. (2002). Brownian motors: Noisy transport far from equilibrium. *Physics Reports*, *361*, 57–265. https://doi.org/10.1016/S0370-1573(01)00081-3

Reimann, P., Grifoni, M., & Hänggi, P. (1997). Quantum ratchets. *Physical Review Letters*, *79*, 10–13. https://doi.org/10.1103/PhysRevLett.79.10

Risken, H. (1989). *The Fokker–Planck equation*. Springer: Berlin. https://doi.org/10.5772/9730

Sakurai, A., & Tanimura, Y. (2011). Does $\hbar$ play a role in multidimensional spectroscopy?

Shit, A., Chattopadhyay, S., & Chaudhuri, R. (2012). Quantum escape in the presence of a time-periodic oscillating force. *Europhysics Letters, 97*, 40006(1–5). https://doi.org/10.1209/0295-5075/97/40006

Shit, A., Chattopadhyay, S., & Ray Chaudhuri, J. (2011). Effective quantum Brownian dynamics in presence of a rapidly oscillating space-dependent time-periodic field. *Physical Review E, 83*, 060101(R)(1–4). https://doi.org/10.1103/PhysRevE.83.060101

Shit, A., Chattopadhyay, S., & Ray Chaudhuri, J. (2013). Quantum stochastic dynamics in the presence of a time-periodic rapidly oscillating potential: Nonadiabatic escape rate. *Journal of Physical Chemistry A, 117*, 8576–8590. https://doi.org/10.1021/jp402565y

Tanaka, M., & Tanimura, Y. (2009). Quantum dissipative dynamics of electron transfer reaction system: Nonperturbative hierarchy equations approach. *Journal of the Physical Society of Japan, 78*, 073802(1–4). https://doi.org/10.1143/JPSJ.78.073802

Tanaka, M., & Tanimura, Y. (2010). Multistate electron transfer dynamics in the condensed phase: Exact calculations from the reduced hierarchy equations of motion approach. *Journal of Chemical Physics, 132*, 214502(1–11). https://doi.org/10.1063/1.3428674

Tanimura, Y. (2006). Stochastic Liouville, Langevin, Fokker–Planck, and master equation approaches to quantum dissipative systems. *Journal of the Physical Society of Japan, 75*, 082001(1–39). https://doi.org/10.1143/JPSJ.75.082001

Tanimura, Y. (2012). Reduced hierarchy equations of motion approach with Drude plus Brownian spectral distribution: Probing electron transfer processes by means of two-dimensional correlation spectroscopy. *Journal of Chemical Physics, 137*, 22A550(1–9). https://doi.org/10.1063/1.4766931

Tanimura, Y., & Ishizaki, A. (2009). Modeling, calculating, and analyzing multidimensional vibrational spectroscopies. *Accounts of Chemical Research, 42*, 1270–1279. https://doi.org/10.1021/ar9000444

Tanimura, Y., & Wolynes, P. G. (1991). Quantum and classical Fokker-Planck equations for a Gaussian-Markovian noise bath. *Physical Review A, 43*, 4131–4142. https://doi.org/10.1103/PhysRevA.43.4131

Tanimura, Y., & Wolynes, P. G. (1992). The interplay of tunneling, resonance, and dissipation in quantum barrier crossing: A numerical study. *Journal of Chemical Physics, 96*, 8485–8496. https://doi.org/10.1063/1.462892

Tsekov, R. (1995). Dissipation in quantum systems. *Journal of Physics A: Mathematical and General, 28*, L557–L561. https://doi.org/10.1088/0305-4470/28/21/007

Tsekov, R. (2007). Comment on 'Semiclassical Klein−Kramers and Smoluchowski equations for the Brownian motion of a particle in an external potential'. *Journal of Physics A: Mathematical and Theoretical, 40*, 10945–10947. https://doi.org/10.1088/1751-8113/40/35/N01

Weiss, U. (2012). *Quantum dissipative systems* (4th ed.). World Scientific Publishing Company: Singapore. https://doi.org/10.1142/8334

Zwanzig, R. (2001). *Nonequilibrium Statistical Mechanics*. Oxford University Press: New York.