

Ph.D. Synopsis of
Analytical solutions of quantum & statistical multi-state
models in time-domain

A Thesis

To be submitted by

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for the award of degree of

Doctor of Philosophy



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October, 2020

1. Introduction

Understanding molecular processes forms the basis of understanding several natural processes that we come across in everyday life. Some examples such as, vision transduction by eyes, chemical reactions, mechanisms of solar/electrochemical batteries, life-making reactions such as photosynthesis and glycolysis, understanding and making of (molecular) electronic devices etc.. Across the disciplines of physics, statistical physics and quantum physics have so far introduced few tools in order to understand these molecular processes. Molecular processes in general, can be understood as crossing between different energy states which are achieved through change in configurations such as bond length, bond angle, polarization, etc. of the molecule. Taken that a process as effectively one-dimensional (along the steepest descent change of energy), a relevant configuration that changes during the molecular process is taken to be x . A complete Hamiltonian description that accounts for each electrons, ions for the many-body molecular processes gives rise to a set of Born-Oppenheimer surfaces which can be derived for the corresponding axis x [1, 2]. Molecular processes inside gaseous phase such as spectroscopic transitions, chemical reactions, etc. can be understood as the wave-packet transfer between the Born-Oppenheimer surfaces as expressed by [3, 1, 2],

$$\begin{pmatrix} \hat{H}_{11} & V_{12}(x,t) \\ V_{21}(x,t) & \hat{H}_{22} \end{pmatrix} \begin{pmatrix} \Psi_1(x,t) \\ \Psi_2(x,t) \end{pmatrix} = i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \Psi_1 \\ \Psi_2 \end{pmatrix}, \quad (1)$$

where \hat{H}_{ii} is the Hamiltonian governing the initial (say 1), and final state (2). The non-diagonal terms $V_{12}(x,t)$ and $V_{21}(x,t)$ are called the non-adiabatic coupling operators that induce $1 \rightarrow 2$ and $2 \rightarrow 1$ transitions respectively. Here the final and initial states of the molecule will be represented by a corresponding probability amplitude $\Psi_i(x,t)$. The form of the Hamiltonian operator is expressed as, $\hat{H}_{ii} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U_i(x)$ where U_i are the diabatic potential energy of different states. Such multi-state equations of quantum mechanics when modeled appropriately can explain electronic transitions [4], chemical reactions [5], electron transfer [2], etc.. Many nuclear scattering processes are also theoretically similar to the molecular processes [6]. Once, the wavefunctions are known, the time-dependent population profiles of each states can be evaluated using the formula:

$$P_i(t) = \int_{-\infty}^{\infty} dx |\Psi_i(x,t)|^2.$$

Or alternatively, the Laplace/energy-domain wavefunctions can be used to evaluate the Raman spectra and electronic absorption spectra using the following respective equations:

$$I_R \propto \left| \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx_0 \Psi_f^*(x,0) iG(x,x_0;\omega+i\Gamma) \Psi_i(x_0,0) \right|^2, \quad (2)$$

$$\text{and } I_A \propto \text{Re} \left\{ \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx_0 \Psi_i^*(x,0) iG(x,x_0;\omega+i\Gamma) \Psi_i(x_0,0) \right\}. \quad (3)$$

Whereas, when the molecule is immersed in a solution, the molecular motion will be highly coupled to the solvent forces. It will be a many-body system that constitutes the molecule of interest that is surrounded by Avagadro's order of solvent molecules. Hence a complete description that includes all the solvent molecules is impossible, yet an approach that assumes a random (Brownian) motion of molecular configurations can be undertaken. Such an approach is called the reaction-diffusion approach for understanding reactions inside condensed phases [7, 8]. Using

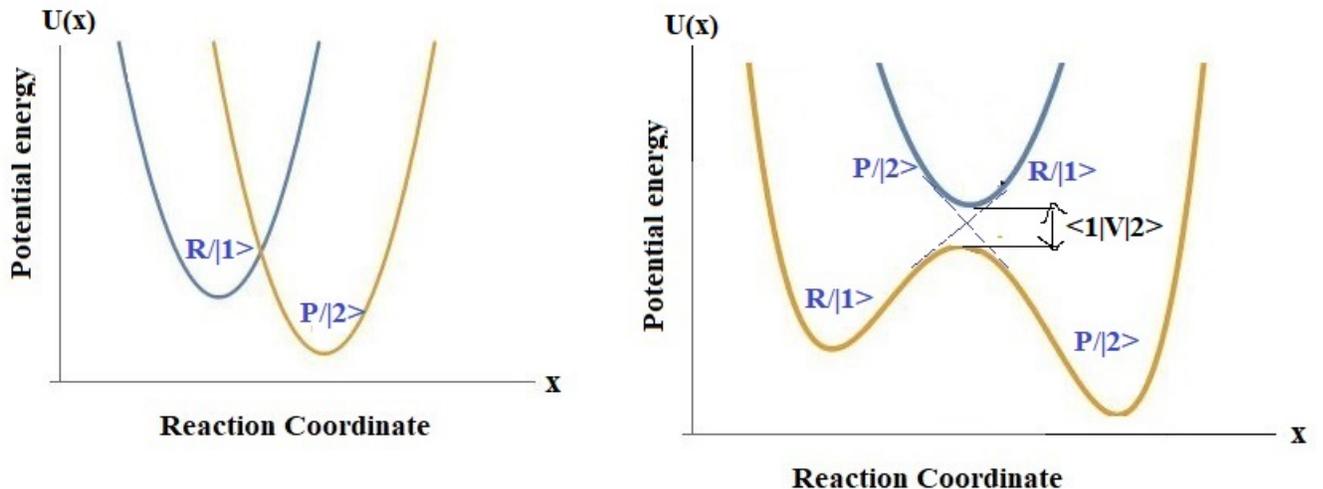


Figure 1: Schematic one-dimensional description of a molecular process as a curve crossing between Born-Oppenheimer surfaces. The denotations R and P indicate reactants and products while |1) and |2) represent different quantum states. The process proceeding as in scheme (a) is called diabatic representation, while the process happening through scheme (b) is adiabatic representation of the process.

a similar description as in the gaseous phase, the reaction can be described as crossing between Born-Oppenheimer surfaces. The only difference is a change in the equation of motion that will govern the initial and final state of the molecular process. The multi-state model explained by statistical mechanics is given by

$$\begin{pmatrix} \mathcal{L}_{11} - S_1(x, t) & S_2(x, t) \\ S_1(x, t) & \mathcal{L}_{22} - S_2(x, t) \end{pmatrix} \begin{pmatrix} P_1(x, t) \\ P_2(x, t) \end{pmatrix} = \frac{\partial}{\partial t} \begin{pmatrix} P_1(x, t) \\ P_2(x, t) \end{pmatrix}, \quad (4)$$

Where the \mathcal{L}_{ii} are the Smoluchowski operators of corresponding states and $S_i(x, t)$ are the non-adiabatic couplings that induce transition between the states. The $P_i(x, t)$ represents the probability distribution function over the molecular configuration at any time t corresponding to initial and final states. The Smoluchowski operators are expressed as, $\mathcal{L}_{ii} = D_i \frac{\partial^2}{\partial x^2} + \frac{\partial}{\partial x} P(x, t) \frac{d}{dx} U_i(x)$. The solvent parameters are incorporated into model through the D_i 's as expressed by, $D = \frac{k_B T}{\zeta}$. Here T denoted the temperature of the solvent bath, and ζ denotes the viscosity of the condensed phase. The $U_i(x)$ are molecular potentials corresponding to the reactant and product states. The survival probability expressed by, $Q_i(t) = \int_{-\infty}^{\infty} P_i(x, t) dx$ gives the respective concentration of reactants and products. Or alternatively, the asymptotic Laplace domain solutions can provide the first order concentration profiles with an average rate constant k_I and a long time rate constant k_L expressed by,

$$k_I = \frac{1}{Q(s=0)}, \quad k_L = -\text{pole of } Q(s) \text{ near } s = 0 \text{ respectively.}$$

In this thesis, we develop mathematical methods to solve multi-state problems of quantum mechanics and statistical mechanics in time-domain. Our solutions could serve as time-dependent profiles for studying molecular processes in gaseous and condensed phase.

2. Motivation & Objectives

Regarding the multi-state problems of quantum mechanics, the exact non-adiabatic wavefunctions $\Psi(x, t)$ are unavailable even for simple models of Eq. 1 [3, 9]. So far, mathematical methods were developed to obtain the approximate/asymptotic solutions that were further useful in calculating related entities such as transition probability,

etc.. The importance of the problems was realized following the influential work done by Landau [4, 10], Zener [11], and Stuckelberg [12]. The contextual importance and the lack of mathematical methods were immediately realized leading to updations given by Rosen [13], Demkov et al. [14, 15, 16, 17], Osherov et al. [18, 19, 20, 21], H. Nakamura et al. [22, 23, 24], and M. S. Child [25] etc.. The updations included introducing new models or improving the available approximate expressions of transition probability or other analytical entities. The models related to delta-function coupling between the states were considered by Chakraborty et al. [9, 26, 27, 28, 29, 30] and their analytical attempts involve Laplace/Fourier transformations. They were able to provide upto the Laplace/energy-domain solutions of the wave packet dynamics, and beyond which the solutions are not invertible to time-domain. Whereas, the time-domain solutions can serve as molecular profiles for studying such processes dynamically.

Regarding the reaction-diffusion approach on molecular process modeled by statistical physics, the formalism was well-known since the original work of H. A. Kramers [7, 31]. Those models can be classified into two types: 1) the reaction proceeds by overcoming an activation barrier (equivalent to the adiabatic representation of molecular process, Refer Fig. 1a), 2) where the reaction proceeds by curve crossing between states (diabatic representation, Fig. 1b). Regarding the type 1, some effective models [32, 33, 34] consider a finite barrier during the reaction propagation. Such models [32, 33, 34] have been solvable only in the Laplace domain and are still open to solve in time-domain . They constitute a class of multiple boundary problems that share the same mathematical complexity of transcendental Laplace/Fourier domain solutions. A method developed to solve either of the models can solve all the other multiple boundary problems as well.

Regarding the reaction-diffusion models of type 2, so far no two-state models have been reported for an exact solution and only Laplace domain solutions are available so far [35, 36, 37, 38, 39]. Such two-state models can be used to study reversible reactions, electronic relaxation, and electron transfer processes, polymer looping etc. with an explicit consideration of all the states. For an multi-state model as expressed by Eq. 4, in the limit of $S_1 \gg S_2$, they can be effectively described by a single Smoluchowski operator in presence of a sink given by the exit condition $S_1(x, t)$ [40]. In such descriptions, the consideration of the other states are implicit. For models even in this reductionized limit, the time-domain solutions are available only if the potential either had a translational symmetry [41] or if the problem has a mirror symmetry about the trap [42, 43]. For a problem, when the effect of molecular potentials are considered without the mirror symmetry about trap, the solution are so far available only in the Laplace domain [44, 45, 43, 46] and such a model possess rich insights into reactions based on the interplay between parameters.

The main objective of this research work is to develop mathematical methods to solve the above-mentioned insightful models of statistical mechanics and quantum mechanics. The resulting time-domain solutions would improve the understanding over molecular processes that happens inside gaseous/condensed phases. Also using the experience from the analytical approaches, we are able to propose future prospects of introducing efficient algorithms to solve for generalized models of both statistical mechanics and quantum mechanics.

3. Description of the Research Work

In the thesis, various problems with diverse mathematical complexities were attempted as can be understood from the elaboration in the subsequent subsections. The proposed methods differ even between different problems of the same subsections. However, we find it convenient to have the following expression of a generic method, that will be useful to explain different problems specifically through a general expression. The partial differential equation of interest in the thesis (be it a Smoluchowski or Schrödinger), can be expressed as the following,

$$\frac{\partial y(x, t)}{\partial t} = (\mathcal{L} - S(x))y(x, t), \quad (5)$$

where \mathcal{L} is a differential operator and other space-dependent terms can be clubbed into $S(x)$. The solution of such an equation can be expressed as the following,

$$y(x, t) = e^{(\mathcal{L} - S(x))t}y(x, 0) \quad (6)$$

The initial data $y(x, 0)$ can be written as the inversion of its Fourier-transformed version $\tilde{y}(k, 0)$ as shown,

$$y(x, 0) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{y}(k, 0)e^{ikx} dk. \quad (7)$$

In general, the above expansion is not limited to Fourier transformation. It would be convenient to use the basis transformation which is the eigenfunction of \mathcal{L} operator. This choice will simplify the expansion of $e^{\mathcal{L}t}$ which will be required in the following equation.

$$y(x, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{y}(k, 0)e^{\mathcal{L}t}p(x, k)dk. \quad (8)$$

The $p(x, k)$ in the above equation will be called the kernel for a considered problem. The kernel in principle contains the effect of boundaries ($S(x)$) and the effect of potentials incorporated into it. They can be systematically derived by solving the time-independent form of the \mathcal{L} operator.

3.1. *Mathematical method development for diffusion problems having single boundary*

In this work, we developed a method to solve a heat equation with a single δ -function sink. Choosing the flat potential highly simplifies the method shown in Eq. 8 into an Fourier-inversion of stationary distribution. The obtained solution satisfies the original equation, boundary conditions. They match with the numerical results and also with the available solutions under limiting cases [41, 47, 48]. The solution was transformed to solutions of other unsolved problems such as a harmonic potential with a δ -function sink placed arbitrarily, and a $|x|$ -potential with sink placed at its minima. These solutions were also verified analytically and numerically. Analytical and numerical verifications of all the work are presented through a MATHEMATICA notebook enclosed with the thesis. The use of the theoretical profiles in fitting the experimental relaxation data of tri-phenyl methane dye is also shown.

3.2. *Mathematical method development for diffusion problems with multiple boundary: An universality class of problems*

For a diffusion problem having single Smoluchowski operators, the models such as: A) V-potential with a sink given by, $U(x) = b|x + x_m|$ with $S(x, t) = k_0\delta(x - x_m)$, B) $U(x) = \theta(-x)|x + x_m| + \theta(x)(x_m - x)$, C) the bucket

potential, $U(x) = \theta(|x| - x_m)(x - x_m)$, etc. involve two boundaries at $x = -x_m, x_m$ respectively. All problems that involve more than a single boundary share a similar trait that their corresponding Laplace/Fourier kernels would involve a transcendental denominator that leads to insolubility analytically. A method developed for a single problem can be used to solve several such multiple boundary problems. This facilitates solving an arbitrary potential problem getting resolved into a piece-wise linear problem with multiple boundaries. As an initial contribution, we developed a time-domain method to solve a simple heat equation in presence of two sink boundaries (called as ‘‘Oster-Nishijima’s model’’). The choice of flat potential significantly reduced the mathematical complexities other than the transcendental nature of the kernels. Then the kernel $p(x, k)$ was solved for $C = 1$ consideration instead of following the conventional $A = 1$ consideration. Now this consideration also overcame the transcendental nature of the poles, and therefore admitted a time-domain solution that obeys the original equations and the boundary conditions. However, the solution’s accuracy is limited to particular parametric regimes due to the $C = 1$ consideration. Now the models A and B were decomposed into a heat equation in presence of two-sinks using suitable transformations. The time-domain solution were obtained for the models A and B which undergoes all the solution test as well as continuity and derivative requirements. However, the disadvantage of the Oster-Nishijima’s solution pass on to the solution of models A and B and hence they differ from the numerical inversion of available Laplace domain solutions. So we conclude that solving the Oster-Nishijima’s model for $A = 1$ consideration instead of $C = 1$ consideration will help in solving a class of multiple boundary problems which are longstanding open problems [32, 49, 50, 33] in this field and are highly insightful [34].

3.3. *Mathematical method development for diffusion dynamics between coupled-states*

So far, by solving a single operator of Smoluchowski equation we considered only the effect of reactant/excited state in context of reactions/electronic relaxation respectively. Such a single-state description is valid only in the limit of $S_1 \gg S_2$. So far, the explicit effect of ground/product state has never been solved in time-domain for any model [35, 39, 51]. In our work, we have extended our time-domain method to solve two-state models of two types: i) a model as considered in Refs. [35, 52, 53] is an open system, ii) a closed two-state model which are useful in the context of reversible molecular processes [39, 38]. Our works on model (ii) gives re-realization of original concepts like Le Chatlier’s principle, dynamic equilibrium, equilibrium constant, etc. resulting naturally from the statistical two-state description.

3.4. *Analytical solution for a new quantum scattering model*

In this work, we develop a method to solve the time-dependent Schrödinger equation for a scattering process. So far, other than the Dirac’s delta potential barrier, the exact wave-packet dynamics are not reported for any other scattering models analytically. Here, we develop the analytical solution of $\Psi(x, t)$ for a rectangular barrier when it has an ultrashort width. Also it is to note that in the ultrashort width limit, the results are generic and the shape of the barrier does not matter [54]. The statistical properties of the wave-packet are studied and discussed in detail.

3.5. *Mathematical method development for multi-state quantum scattering process*

In this work, we study multi-state Schrödinger equations when the coupling functions are given by Dirac delta functions/constants. Using the method developed to solve constantly coupled equations, we classify two-state

models of two types: 1) one in which the population transfer happens through oscillations, 2) one in which the population transfer happens through decay. The models of type 1 are useful in studying the vibrational transitions in a molecule, and the model 2 is useful in studying the electronic transitions. However, in the context of electronic transitions, it is useful to solve a coupling that is localized in space. So we solve the two-state models of these two types for the Dirac delta coupling as well. The wave-packet dynamics at different time are plotted and discussed in detail.

3.6. Conclusions

The thesis introduces novel mathematical methods to solve partial differential equations of interest in statistical and quantum physics. We start with a simple model when the potential energy is flat and through appropriate transformations solve various unsolved problems in time-domain. We have proposed various time-domain profiles to study molecular processes in gaseous phase and condensed phase as a function of system and molecular parameters.

4. Outline of the thesis

This thesis consists of 2 main chapters (**Chapters 2-3**) along with an introductory chapter (**Chapter 1**), and a chapter (**Chapter 4**) describing the overall conclusion and future scope. The suborganization of the thesis chapter are described below: **Chapter 1** introduces multi-state models for molecular processes inside gaseous and condensed phases, starting from the full Hamiltonian description. The generalized model equations are introduced and the literature review of available analytical solutions are presented. Further we pose the analytical models considered in this thesis while discussing their importance in various fields of science and engineering. In **Chapter 2**, we propose time-domain methods for single-state problems as a first section. The open problems such as when the diabatic potentials are given by $U(x) = b|x|, \frac{1}{2}kx^2$ are solved by a transformation from a simple problem of flat potential with δ -function sink. The solution of parabolic potential with sink was used to fit the experimental data of dye relaxation that is available in Ref. [55]. In the second section, we develop time-domain method to solve two-state models. A two-state model as considered in Ref. [35] is solved for the flat diabatic potentials. Following, a closed two-state system is solved that gives its insights into reversible reactions, electron transfer, and to electronic relaxation process. The analytical results revisits original concepts of reversible processes resulting naturally from the statistical description. In **Chapter 3**, we develop time-domain methods to solve quantum scattering problems. We introduce the algebra to solve the wave-packet dynamics interacting a rectangular barrier of ultrashort width. The importance of such models is known since a long time [56]. Following, we apply our time-domain method to a quantum two-state model coupled through a δ -function. Next we solve a series of identical potentials of any shape that are coupled by constant couplings. Interesting insights emerge on the two-state models based on different parameters. Using the work, we classify general two-state models into two types: 1) one in which the population exchange happens through oscillation, 2) another in which the population exchange happens through the decay. In the following section, we solve a model of type 2 when coupled through δ -functions. **Chapter 4** summarizes the main contribution of the research work, along with the scopes for future research.

LIST OF PUBLICATIONS

Journal Publications

1. **R. Saravanan***, A. Chakraborty, Reaction-diffusion system: Fate of a Gaussian probability distribution on flat potential, *Physica A: Statistical Mechanics and its Applications*, 536 (2019), 120989, <https://doi.org/10.1016/j.physa.2019.04.225>.
2. **R. Saravanan***, A. Chakraborty, Exact diffusion dynamics of a Gaussian distribution in one-dimensional two-state system, *Chemical Physics Letters*, 731 (2019), 136567, <https://doi.org/10.1016/j.cplett.2019.06.064>.
3. **R. Saravanan***, A. Chakraborty, Some exact time-domain results related to reversible reaction-diffusion systems, *Chemical Physics*, 539 (2020) 11095, <https://doi.org/10.1016/j.chemphys.2020.110955>.
4. **R. Saravanan***, A. Chakraborty, Exact diffusion dynamics in the presence of two competing sinks: Analytical solution for Oster-Nishijima's model, *Physica A: Statistical Mechanics and its Applications*, 563, 125317, <https://doi.org/10.1016/j.physa.2020.125317>.

Communicated Work

1. **R. Saravanan***, A. Chakraborty, A general method to solve diffusion in piece-wise linear potentials in the time-domain.
2. **R. Saravanan***, A. Chakraborty, Exact time-domain solution of the Schrödinger equation for a new scattering model.
3. **R. Saravanan***, D. Kumar, A. Chakraborty, An exact analytical scheme using a new potential to solve one-dimensional quantum systems.
4. **R. Saravanan***, A. Chakraborty, Exact solution for a reaction-diffusion system with an attractive harmonic well.

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