Analytical Solutions of Quantum & Statistical Multi-State Models in the Time-Domain

A Thesis Submitted by

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for the award of the degree of

DOCTOR OF PHILOSOPHY

SCHOOL OF BASIC SCIENCES

INDIAN INSTITUTE OF TECHNOLOGY MANDI.

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Wednesday 2nd June, 2021

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DECLARATION BY RESEARCH SCHOLAR

I hereby declare that the entire work assimilated in this thesis entitled **Analytical Solutions of Quantum & Statistical Multi-State Models in the Time-Domain** is the result of investigations carried out by **me** in the **School of Basic Sciences, Indian Institute of Technology Mandi**, under the supervision of **Dr. Aniruddha Chakraborty**, and that it has not been submitted elsewhere for any degree or diploma. In keeping with the general practice, due acknowledgments have been made wherever the work described is based on finding of the other investigators.

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THESIS CERTIFICATE

This is to certify that the thesis titled **Analytical Solutions of Quantum & Statistical Multi-State Models in the Time-Domain**, submitted by **Saravanan Rajendran**, to the Indian Institute of Technology, Mandi, for the award of the degree of **Doctor of Philosophy**, is a bonafide record of the research work done by him under my supervision. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

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ACKNOWLEDGEMENTS

I feel highly grateful to be supervised by Dr. Aniruddha Chakraborty and would like to thank him for the kind, motivating, and enlightening times he spent for me throughout the duration. All his efforts to introduce me to various opportunities were bringing the best during the Ph.D. duration. The gratitude extends to Dr. Suman Kalyan Pal, Dr. Subhajit Roy Choudhury, Dr. Pradeep Kumar, Dr. Prashanth P Jose, as DC members and also as course teachers. Their valuable inputs influenced various sections of the thesis, and their support in my progress mattered a lot. I would fondly remember the opportunity I got to visit ICTP and thanks remain to Dr. Pradeep Kumar and Dr. Aniruddha for facilitating it. Sincere thanks are conveyed to lab friends Moumita Ganguly, Chinmoy Samanta, and Swati Mudra for their friendship and support. I would like to thank all the other junior lab mates, interns who contributed throughout the learning in Ph.D. I am grateful to have my friends Mothi Kailash, Amudhan Muthaiah, Vignesh, Ruchika Mahajan, Balaji Ramachandran, V. Maivizhikannan, Mohnish Pattathurajan who made it a wonderful stay far from home. Extreme gratitude extends to my sister Ms. R. Umadevi for her support throughout all my tough times. I would like to thank the people of IIT Mandi who were of support during the stay directly and indirectly. Ultimately, I would like to express gratitude towards the supreme nature that made this possible which is complex and thereby making it a career to work on it.

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ABSTRACT

KEYWORDS: *Mathematical methods, non-equilibrium statistical physics, quantum scattering, time-domain methods, coupled-partial differential equations (PDEs), multi-state problems, molecular processes, non-adiabatic transitions, reaction-diffusion systems, condensed-phase chemical dynamics, stochastic processes, Schrödinger equation, Smoluchowski equation, Brownian motion, spectroscopic and collision processes, complex systems.*

Multi-state systems that undergo non-adiabatic transitions between various states can mimic several complex processes in nature. The notion is an interdisciplinary concept and is useful across various disciplines of science. The theory of complex systems often can be derived using statistical physics or quantum physics. In particular, multi-state models are used as a fundamental tool for understanding molecular processes happening in gaseous, liquid phases, and sometimes in solid phases as well.

Molecular processes, in general, can be understood as crossing between different energy states of the molecule which are achieved through a change in configurations such as bond length, bond angle, polarization, etc. of the molecule. If the molecule is in the gaseous phase, a complete Hamiltonian description that accounts for each electron, ions for the many-body molecular processes gives rise to a set of Born-Oppenheimer states that are coupled. Examples such as spectroscopic transitions, chemical reactions, etc. can be understood as the wave-packet transfer between these Born-Oppenheimer surfaces. Taken that the process is effectively one-dimensional (along the steepest descent change of energy), the relevant configuration that changes during the process is taken to be x, hence simplifying the models. Now, the process can be studied using one-dimensional coupled-Schrödinger equations which incorporates the shape of the energy states $U_i(x)$ and the couplings $V_{ij}(x)$ that induce the $i \to j$ state transitions in the molecule. Once the time-dependent wave functions $\Psi_i(x,t)$ are derived, the population profiles of each state and other spectral profiles can be calculated. Regarding such

models, the exact non-adiabatic wave functions $\Psi_i(x,t)$'s are unavailable even for simple two-state models. So far, the mathematical methods were developed to obtain the approximate/asymptotic solutions in order to further calculate related entities such as transition probability, etc. The importance of the problems was realized following the influential work done by Landau, Zener, and Stueckelberg. The contextual importance and the lack of mathematical methods were immediately realized leading to updations given by Rosen, Demkov, et al., Osherov, et al., H. Nakamura et al., and M. S. Child, 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. and their analytical attempts involve Laplace/Fourier transformations. They were able to provide up to the Laplace/energy-domain solutions of the wave packet dynamics, and beyond which the solutions were not invertible to time-domain. As there have been no full-time-domain solutions available so far for δ-coupled models, there becomes an importance to solve them in time-domain in order to study gas-phase processes dynamically.

Whereas when the molecule is immersed in a solution, the molecular motion will be highly coupled to the solvent forces. A complete description that includes all the solvent interactions is impossible, yet an approach that assumes a random (Brownian) motion of molecular configurations can be undertaken. The process can be characterized as a transition between different Born-Oppenheimer surfaces as similar to gas-phase description. Hence the probability distribution over molecular configuration over time i.e., $P(x,t)$ is governed by coupled-Smoluchowski equations in 1D. The advantage of using the Smoluchowski equation is that system parameters such as temperature, the viscosity of the solvent bath, excitation parameters, and molecular parameters such as potential, molecular configurations are inbuilt in the model. The solution profiles can be useful in studying chemical kinetics, for understanding and predicting reaction data as a function of parameters, which is otherwise a tedious job to obtain the multi-parametric fitting function. Such reaction-diffusion models have only Laplace domain solutions and do not have a time-domain solution unless the problem involves translational or mirror symmetry. The Laplace domain solutions can give only first-order rate constants at different time regimes. On the other hand, a time-domain work would give exact con-

centration profiles without assuming the order of the reaction. In this thesis, we develop mathematical methods to solve various Smoluchowski models in the time domain. In the end, we present exact time-dependent concentration profiles as a function of the system and molecular parameters for reactions in condensed phases.

The main objective of this research work is to develop mathematical methods to solve some insightful models of statistical mechanics and quantum mechanics analytically. The resulting time-domain solutions would improve the understanding over molecular processes that happens inside the gaseous/condensed phase. 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. The thesis is organized as follows: Chapter I gives a detailed introduction to the arisal of multi-state problems in nature and poses some of the useful models. In chapter II, we give our time-domain method to solve various reaction-diffusion models given by the Smoluchowski equation. The appropriate analytical and numerical verifications are presented in the respective sections. In chapter III, we apply the methods to solve scattering and multi-state problems in quantum physics (Schrödinger operators). Chapter IV concludes the thesis by stating possible considerations over the present work and the scope of the work in the future.

TABLE OF CONTENTS