



MONASH University

Resonance energy transfer for optoelectronics

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Summary

Energy gaps are created in chemical and biological systems due to quantum effects. These energy gaps can be used to absorb and store energy from sun by means of photons. In photosynthesis, this captured energy is transferred from absorbing antenna to the reaction centre by an energy transfer process known as Excitations Energy Transfer(EET). EET in photosynthesis is one of the highly researched areas in science. The main research attraction for this transfer process is the fact that it is highly efficient which can be utilized in potential applications if understood properly.

EET is understood in the incoherent regime where the excitations are localized upon transferring to the acceptor chromophore. In this domain, not only a quantum model of this system can be used to elucidate and simulate the energy transfer, but also a semi classical or a pure classical model is capable of explaining the EET dynamics. When EET falls under the coherent regime, is yet to understand completely where quantum effects are more visible.

Quantum coherence effects in light harvesting systems play an integral role during the energy transport process. These effects, when they are large enough, aid to maximize the energy transfer among the chromophores in the energy transferring paths. In addition, they are also resourceful in redirecting excitons to alternative paths when they are trapped in energy barriers. In this thesis, our focus is to use such advantages of coherent resonance energy transfer dynamics to improve the energy transfer processes in optoelectronics and nano-photonics systems.

Exploration of current knowledge base of energy transfer processes reveals the significant role of surrounding quantum environment plays in them. In fact, current quantum environments are simulated utilizing exponential terms and log functions are quite accurately describe most environments. But, contemporary spectral density functions characterizing quantum environments, lack the ability to delineate environments which are slightly deviated from the standard forms. This knowledge gap naturally provided us the motivation to look into such systems. In this study, we impart on energy transferring processes of quantum systems which are attached to such quantum environments.

We analyse how slight deviations from standard ohmic-like environments can affect the quantum coherent effects utilizing positive logarithmic perturbations for a donor-acceptor chromophoric system. In addition, we have investigated how donor-acceptor coupling and system-bath coupling influence the exciton transport dynamics of these quantum systems. The energy transfer process was simulated employing the well established, elegant and highly diverse variational polaron and full-polaron transformation methods. This analysis has been extended to multi-site systems which are closer to real world systems. Since logarithmic perturbation factors can be both positive and negative, our analysis also investigates the effect of negative factors along with a comparison of full-polaron and variational polaron transformation methods.

Findings of these studies are essential in understanding and characterizing the energy carry over in excited quantum systems. Further, they could open up new research avenues and also potential applications in enhancing, inducing, controlling and reducing quantum coherence in energy transfer process of artificial light harvesting systems which use optoelectronics.

General Declaration

This thesis contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

Nisal Sankalpa De Silva

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Publications During Enrolment

- Nisal De Silva, Malin Premaratne, Tharindu Warnakula, Sarath D Gunapala and Mark I Stockman. **Effect of logarithmic perturbations in ohmic like spectral densities in dynamics of electronic excitation using variational polaron transformation approach.** J. Phys.: Condens. Matter 33 145304, Feb. 2021;
- Nisal De Silva, Malin Premaratne, and Tharindu Warnakula. **Coherent resonance energy transfer dynamics of super-Ohmic environments experiencing logarithmic perturbations using full-polaron transformation-based approach and its performance.** Proc. SPIE 11771, Quantum Optics and Photon Counting 2021, 1177121 (23 April 2021);
- Nisal De Silva, Malin Premaratne, and Tharindu Warnakula. **Multisite exciton energy transfer dynamics in super Ohmic environments experiencing logarithmic perturbations using full polaron transformation-based quantum master equation.** Proc. SPIE 11771, Quantum Optics and Photon Counting 2021, 1177122 (23 April 2021);

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Chapter 1

Introduction

1.1 Background and Motivation

Resonance Energy Transfer (RET) process [1–6] is an integral component of quantum optics which is also a core constituent of quantum physics [7–18]. Owing to its highly efficient nature, RET process has acquired attraction in recent years with the emerging areas such as solar energy harvesting [19–24], information transfer [25, 26], bio sensing [27–29], photosynthetic proteins [30–32], conjugated polymers [8, 9, 33–36], spasers [18, 37–39] and solid quantum dots [4] etc. RET process critically discuss the energy transfer that takes place among a donor chromophore and a prospective acceptor chromophore. Förster Theory [1] which has been around since 1948, is successful in elucidating energy transfer mechanisms transpire in a quantum or classical or semi-classical system where bath's (environment's) influence is strong compared to the donor-acceptor interaction [2–6]. In this premise, concomitant energy transfer falls under the incoherent domain where individual chromophores are excited randomly as delineated through Pauli-type dynamics of probabilities. In the counter domain where donor-acceptor interaction is strong in comparison to the bath's influence on the sites, operates the Redfield master equation [40] which describes the coherent energy transfer. Due to the minimized influence from the surrounding environment, energy transfer transpires in this circumstance demonstrates oscil-

lations which indicates that energy is both pumped into and drained out of the donor and acceptor chromophores during the transfer process.

When bath's influence on sites and interactions between sites are comparable to each other, ensuing energy transfer takes place in between coherent and incoherent regimes. Theories based on second-order perturbation such as modified Redfield theory [41,42], variational polaron transformation-based theory [43,44], full polaron transformation-based theory [45,46] and numerically exact methods such as hierarchical equations of motion [47], density matrix re-normalization group [48], path integral [49] formalism are popular attempts in literature to elaborate the energy transfer occurs under these circumstances. Even-though, numerically exact methods are higher in accuracy, use of second-order perturbation methods are common due to being computationally less expensive specially in researches focused on the multi-site systems. Among the second-order perturbation based methods in relation to multi-site systems, multi-site full polaron transformation-based theory has performed well in super-Ohmic environments [50].

Quantum environment's influence on the considered quantum system is represented through a frequency dependent entity named Spectral Density Function (SDF). Most physically relevant and plausible quantum environments are portrayed by a common Ohmic-like SDF which constitutes an exponential decay. Ohmicity parameter in this SDF primarily governs how it behaves in low frequency modes and when the SDF scales from super-linearly to linearly to sub-linearly in low frequencies, corresponding quantum environment changes from super-Ohmic to Ohmic to sub-Ohmic type environment. Owing to fundamental differences manifest between power laws and logarithmic decay [51], logarithmic factors are used in a novel SDF in an effort to deviate the SDF from its current low frequency response. These logarithmic factors aren't an arbitrary choice, in fact, they are innate in low frequency power law expansion of SDF. Moreover, recently

introduced SDF based purely on logarithmic factors of various orders has exhibited to be more accurate in mimicking experimentally obtained SDFs [52]. In this thesis, we theoretically study quantum environments which are slightly deviated from the standard sub-Ohmic, Ohmic and super-Ohmic categorization utilizing a novel type of spectral density function, first introduced in [51]. We especially examine the energy transfer dynamics of quantum systems, both two-level systems and three-level systems (multisite), attached to such disturbed environments by altering environmental factors as well as system factors. We also critically study how quantum coherence between a donor and an acceptor pair is changing due to these factors and what the possible limits to this observed coherent dynamics are. To simulate the energy transfer process, quantum master equations derived from full polaron theory and variational polaron theory have been employed.

In essence, this thesis reveals that quantum coherence of the energy transfer dynamics of a quantum system attached to a disturbed environment is highly depended on many factors. We have found that particular values of logarithmic perturbation factor, are capable of increasing the quantum coherence of the transfer. Besides, we reveal that larger logarithmic factors can reduce the coherent dynamics and they are even capable of shifting the energy transfer to the incoherent regime.

1.2 Research Aims

Analytical characterization of coherent resonance energy transfer dynamics of a two level system coupled to ohmic-like environments with full polaron transformation approach

Contemporary knowledge related to coherent resonance energy transfer dynamics has studied quantum systems under standard sub-ohmic, ohmic and super-ohmic categorization of quantum environments utilizing numerically exact meth-

ods as well as approximation methods based on second order perturbation theory. Full polaron transformation method is one such approximation method which has shown to be very successful in simulating the transfer dynamics of quantum systems in ohmic environments.

We plan to study the effect on energy transfer dynamics when the surrounding quantum environment is perturbed which deviates the spectral density function of the environment from above common and standard categorization. This deviation is aimed to be obtained by introducing logarithmic perturbations to the standard spectral density function. We aim to analyse a two level donor-acceptor system utilizing a full polaron transformation based quantum master equation. We plan to examine the performance of this quantum master equation in different super-ohmic environments as well as environments with different system-bath coupling strengths. Further, we intend to analyse the coherent energy transfer dynamics manifested through full polaron theory in such environments.

Investigating coherent resonance energy transfer using a quantum master equation in variational polaron frame

In this stage, we aim to extend the work of the previous stage by analysing a two level system coupled to an ohmic like bath, experiencing logarithmic perturbations incorporating a variational polaron transformation based quantum master equation. Contemporary literature suggests that variational polaron transformation is superior to full polaron based transformation in terms of the range of the validity in diverse system-bath coupling regimes. Therefore, we plan to investigate not only super-ohmic environments but also ohmic environments which were not possible to study with full polaron theory.

We intend to explore energy transfer dynamics in super ohmic environments in which the factor of logarithmic perturbations is positive. In ohmic environments, impact on the bath coupling strength will be studied under the same log-

arithmetic perturbations. For this analysis logarithmic factors from 0 to 3 will be considered since most perturbations are slight in nature. Furthermore, we plan to look into the impact on different values of the ohmicity parameter for various values of these logarithmic perturbations to observe if there are any correlations or outliers in simulated dynamics.

Analysing coherent resonance energy transfer of a multichromophoric system under logarithmic perturbations utilizing full polaron based quantum master equation

Even though, two-level systems are considered as building blocks of larger quantum systems, it is interesting to explore how inter system parameters such as inter chromophore interaction and site energy levels impact the energy transfer dynamics of multichromophoric systems. Contemporary literature has studied most multisite quantum systems utilizing the standard spectral density functions. It will be interesting to explore such systems in disturbed quantum environments.

Therefore, our aim in this stage was to analyse a multi-chromophoric system utilizing a multichromophoric full polaron quantum master equation. We plan to perturb the attached quantum environment utilizing logarithmic perturbations. We aim to examine the performance of the quantum master equation in various super ohmic environments and wish to analyse the effects of infrared divergence to the overall simulated dynamics.

Performance of variational transformation based quantum master equation in terms of simulating coherent resonance energy transfer in a multi exciton transport system under logarithmic perturbations

Up to this stage, we have planned to use positive logarithmic factors in order to deviate the spectral density function from its original form. However, it will be interesting to seek how negative factors could impact the transfer dynamics of ex-

cited systems. Further, since variational polaron based quantum master equation is known to perform better in most scenarios, our goal in this stage is to simulate and analyse a multi exciton system using the multi site variant of the said transformation.

Therefore, a system with multiple chromophores coupled to independent and identical baths will be considered at this stage which undergo negative logarithmic perturbations. For this analysis, both super ohmic baths and versions of ohmic bath would be considered. Main objective will be to find configurations and scenarios that can enhance the amount of quantum coherence that system experience as whole. Further, if there are certain values of the logarithmic perturbation factor are capable of reducing the quantum coherence effect, that will also be worth investigating.

1.3 Thesis Outline

This thesis entails seven chapters outlined as follows.

Chapter 1 includes an overview into the research background which also presents an outline of the motivation behind the research. It also includes aims of the research and thesis outline.

Chapter 2 presents a detailed overview of current knowledge base of open quantum systems and contemporary theories studying energy transfer dynamics, both numerically exact methods and second-order perturbation based approximation methods. This chapter also includes the role of quantum coherence in energy transferring paths and its advantages. It also provides an overview of quantum coherence that has been captured by current quantum master equations. In addition, it includes the means of representing quantum environments and how they are vital in understanding overall dynamics of quantum systems. This chapter also elucidates on the importance of resonance energy transfer and

its potential and current applications.

Chapter 3 presents the analysis performed on resonance energy transfer in a two-level system with a full polaron transformation based quantum master equation. This quantum system dissipates energy to the quantum environment perturbed by logarithmic perturbations. The performance of the full polaron based theory is analysed with respect to different ohmicity values and bath coupling strengths.

In chapter 4, we investigate the energy transfer of a two-level system utilizing a variational polaron based quantum master equation. We have incorporated logarithmic perturbations to disturb ohmic like spectral densities and we discuss the significance of said perturbations in quantum systems in designing future applications. Further, this chapter describes on how quantum coherence effects are impacted in super ohmic and ohmic regimes under the frequency domain logarithmic perturbation of the spectral density function.

Chapter 5 discusses an extension of the work presented in the chapter 1, with an analysis of non Markovian dynamics of a multi exciton system. It also discusses the performance of multisite full polaron transformation based quantum master equation in ohmic environments when the perturbation factor is positive.

Chapter 6 provides an analysis of quantum coherence present in a multi exciton system experiencing logarithmic power perturbations using a variational based quantum master equation. Impact on quantum coherence effects of multiple acceptors coupled to independent baths are elucidated in detail. This analysis is done for both ohmic and super-ohmic environments with negative logarithmic perturbation factors in the environment. A comparison between full polaron based results and variational polaron based results in such environments is also included.

Finally, chapter 7 concludes the thesis with a summary of important findings of this research. It will also focus on the current trends and knowledge gaps exist-

ing in the field of nano-photonics which are vital for exploration, in order for the future realization of this technology. In addition, this chapter outlines the future experimental works that are worth exploring which are crucial for solidifying existing theoretical work developed in this research.

Chapter 2

Theory and background of resonance energy transfer

This chapter provides a general overview of resonance energy transfer which includes its background and history. We also discuss the role of quantum coherence in relation to the energy transfer of light harvesting systems in addition to an overview of current theories which are used to describe and simulate energy transfer in quantum systems in ensuing sections. Furthermore, we discuss the necessity of polaron transformation and its theoretical background. We also dive into contemporary quantum environments and their role in energy transfer dynamics. Before we conclude this chapter, we also look at both existing and potential FRET-based applications.

Electronic excitations transfer between molecules, is an area that has attracted prime research interest since the formalization of Förster Resonance Energy Transfer (FRET). Energy transfer from an excited donor to a potential acceptor can be stemmed by means of with or without a photon emission. Therefore, energy transfer naturally divides into two sub categories,

- Radiative energy transfer
- Non-radiative energy transfer.

Radiative energy transfer occurs when a donor chromophore spontaneously emit a photon to an acceptor chromophore in the vicinity and this can be identified as the simplest form of energy transfer. In terms of non-radiative energy transfer

mechanisms, we can identify Coulomb coupling [1,20] and orbital overlap methods [53]. These mechanisms are explained more in detail below.

2.1 Non-radiative Energy Transfer Mechanisms

2.1.1 Dexter Resonance Energy Transfer (DRET)

Dexter Resonance Energy Transfer, or also known as exchange of electrons, was introduced by David L. Dexter [53] in 1953, as a form of near field non-radiative energy transfer mechanisms. When the donor and acceptor are in the proximity of each other, typically around 0.1 nm to 1 nm, concomitant energy transfer typically falls under Dexter resonance energy transfer. In DRET, the donor orbit and the acceptor orbit overlaps each other, which facilitates the excited electron transfer from donor to acceptor. In other words, wave functions of donor and acceptor overlap with each other to facilitate the transfer of energy. While the excited electron of donor transfers to the acceptor, acceptor's ground electron is transferred to the donor as shown in the Figure 2.1. This physical transfer of electrons, is the main difference between the energy transfer transpires via DRET and Coulomb coupling mechanisms. In fact, ideal dipole-dipole approximation is invalid for this region. In other words, while FRET theory emphasis the fact that energy released from the donor stimulates the acceptor's ground state electron to be excited through the Coloumb coupling, Dexter theory states that an exchange of electrons should occur in order to transfer the donor's energy to the acceptor. Figure 2.1 shows the process given by, ${}^1D^* + {}^1A \rightarrow {}^1D + {}^1A^*$, where * denotes the exchanging excited electron. Transfer rate of this short range energy transfer mechanism decays exponentially as distance between donor and acceptor is

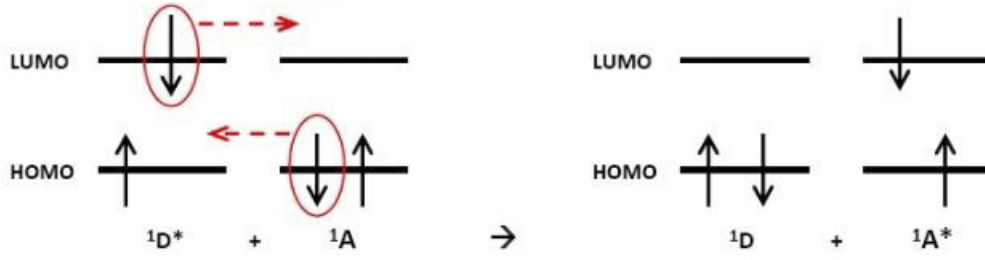


Figure 2.1: Dexter Resonance Energy Transfer Mechanism

increased. This can be written as,

$$TR_{DRET} = JK \exp\left(\frac{-2R_{DA}}{L}\right) \quad (2.1)$$

where J represents the integral of normalized spectral overlap between the donor's emission spectra and the acceptor's absorption spectra. K is a factor unique to the considered donor and acceptor pair, R_{DA} is the distance between the pair and finally, L is the sum of van der Waals radius of the pair.

2.1.2 Förster Resonance Energy Transfer (FRET)

Förster Resonance Energy Transfer (FRET), introduced by Theodor Förster in 1948 [1], is one of the most popular energy transfer processes among the research community. In this method, donor transfers its energy to the acceptor through the dipole-dipole coupling among them. Fermi's golden rule has been used to calculate rate expressions with the assumption of donor and acceptor interaction is weak (weak coupling limit). Transfer rate of FRET is given by,

$$TR_{FRET} = \frac{1}{1 + \left(\frac{r_0}{R}\right)^6} \quad (2.2)$$

where r_0 is the Förster distance (distance between donor and acceptor chromophores where FRET efficiency is 50%) and R is the actual distance between donor and ac-

ceptor chromophores. This form of transfer generally transpires within 2-10 nm from the donor chromophore. There are several requirements to satisfy for FRET to occur between a donor and an acceptor chromophore. They are,

1. Coupling between donor and acceptor should be weak compared to their couplings between the surrounding chromophores,
2. Donor emission spectra and the acceptor absorption spectra should overlap (refer Figure 2.3),
3. Orientation between donor and acceptor dipole moment should not be orthogonal to each other (refer Figure 2.4).

FRET can be realized classically, semi-classically and quantum mechanically since its hopping mechanism is incoherent, which means that once the energy has been transferred to the acceptor chromophore, it will not be returned to the donor chromophore again. Figure 2.2 shows the mechanism of FRET utilizing the virtual photon concept.

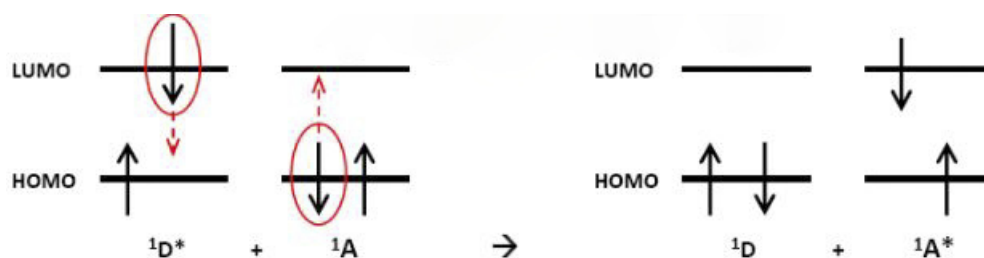


Figure 2.2: Förster resonance energy transfer mechanism

2.2 Quantum Coherence

Extremely efficient light harvesting mechanism in photosynthesis, depends on ultra-fast energy transfer dynamics in excited states and charge separation where quantum superposition and quantum coherent dynamics play a prominent role. In photosynthesis, molecules are congested closely enough to have a significant

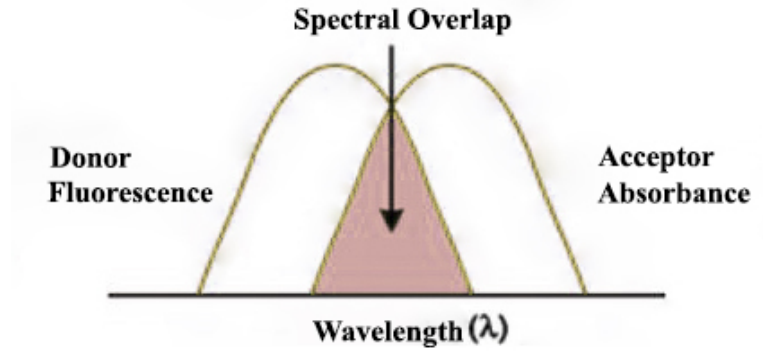


Figure 2.3: Spectral overlap requirement for FRET

coupling among them, in which FRET's assumption of weak coupling is not typically valid. In this type of environment, energy transfer appears to be in the coherent regime where energy bounces back and forth between donor and acceptor chromophores.

Now, let's look at quantum coherence in more detail. To describe coherence effects, let's investigate the wave function given by Eq. (2.3), where a and b are arbitrary constants and, $\hbar\omega_1$ and $\hbar\omega_2$ are exciton energies of e_1 and e_2 , which are the only states of the system.

$$|\psi(t)\rangle = ae^{-i\omega_1 t} |e_1\rangle + be^{-i\omega_2 t} |e_2\rangle \quad (2.3)$$

Next, using the bra-ket notation we construct the system density matrix which results in,

$$|\psi(t)\rangle \langle\psi(t)| = \begin{pmatrix} |a|^2 & a^* b e^{-i(\omega_1 - \omega_2)t} \\ b^* a e^{-i(\omega_2 - \omega_1)t} & |b|^2 \end{pmatrix}. \quad (2.4)$$

Diagonal elements of the density matrix are known as population whereas the off diagonal elements are known as coherences. It's clear from the matrix, the fact that population elements are stationary and coherences are dynamic. These coherences are wave like dynamics which exponentially decay as the time goes by. Therefore, quantum coherence are dominating in the initial stages of exciton gen-

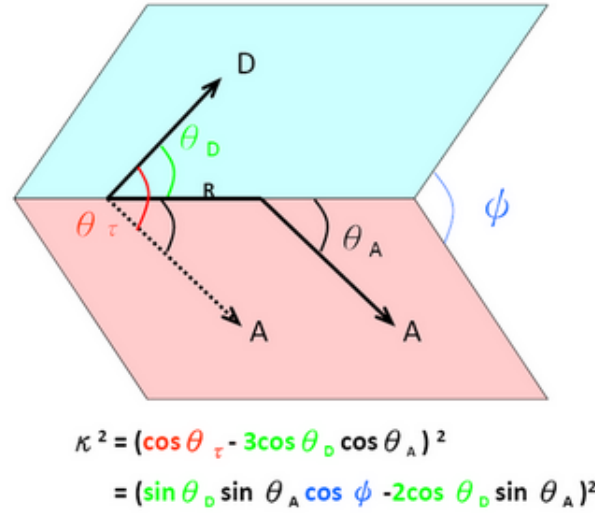


Figure 2.4: Orientation requirement for transition dipoles in FRET. Here, κ^2 represents the orientation parameter which provides a measure of the interaction between dipole moments of the donor-acceptor pair.

erations at a chromophore or an antenna. When coherence is present, eigen states of the system are said to be de-localized, which can be well described through the quantum approach. In the ensuing section, we analyse the role of quantum coherence in light harvesting systems.

2.2.1 Role of coherence in RET and its importance

Quantum coherence in right amount is an advantage to the RET. When there are large coherences, there exists a large site coupling among the chromophores, which will restrict the energy oscillations to the excited states. Hence, this may yield very little to no population transfer. On the other hand when there are small coherences, which indicates that system-environment coupling is very large and that will localize the excitons to the initial states without transferring forward. These excitons could eventually dissipate to the environment. Therefore, for a maximum energy transfer, coupling should be in between these two extremes.

Therefore, one role of quantum coherence is to be large enough to maximize the energy transfer between weak and strong coupling limits.

Secondly, quantum coherence can reduce the amount of excitations trapped in local minima of energy in the transfer paths. These minima occur when a chromophore is surrounded by chromophores which have higher energy than itself. Such energy traps are common in the rugged energy landscape of light harvesting systems. Oscillatory behaviour will pop these excitations out of local minima and can redirect into another path. If not for coherence, these trapped excitations would require a pumping event in order to fly over the energy barrier. Figure 2.7 shows such an energy trap that presents in an energy transferring path where BChl 1 site has lower energy than the Baseplate and BChl 2 site. Figure 2.8 demonstrates that when coupling between BChl 1 and BChl 2 sites are large (refer Figure 2.8(i)), a significant amount of excitations is transferred from BChl 1 site to nearby chromophores. When we decrease the coupling between BChl 1 and BChl 2 sites as shown in Figure 2.8(ii)-(iv), energy transfer has pushed to the incoherent regime and when observing the donor BChl 1 population, the amount of excitations transferred to chromophores in the vicinity remain low.

Third role of quantum coherence is to work as an energy transfer rectifier in energy transferring paths. This could be best explained using Figure 2.7. It is notable that Baseplate, BChl 1 and BChl 2 sites have much higher site energy than BChl 3. In fact, the energy gradient is very high between BChl 2 and BChl 3 sites compared to any other pair of sites. If these two sites are weakly coupled compared to their bath coupling strengths, the energy transfer between the pair would occur in the incoherent regime. Such a configuration would restrict the energy backflow from BChl 3 to BChl 2 site, making this transfer irreversible. These energy transfer rectifiers could be used to create high energy barriers in order to facilitate energy flow into certain directions.

Further, as energy is transferred from molecule to molecule along the trans-

fer path, quantum coherence is repeatedly created, destroyed and recreated as shown in Figure 2.5 and Figure 2.6 [54]. However, observed coherence is decaying under two methods when experiments are conducted. Ensemble dephasing occurs where coherence been transferred to the near entangled molecules and microscopic dephasing where decoherence happens which destroys the coherence between entangled states due to the environment effects. In ensemble dephasing coherence is not destroyed as such, but it helps to distribute coherence along the transfer path. This in return reduces the amount of coherence at the system under consideration. Microscopic dephasing suggests that, population transfer dynamics should occur in a short time period before decoherence completely destroys the excitations. These quantum coherences appear in photosynthesis are

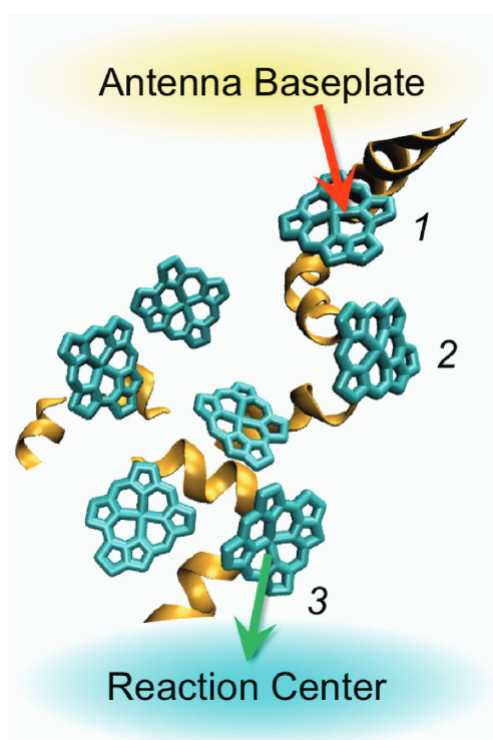


Figure 2.5: Figure shows the structure of the sites. Initial excitation is at site 1. (Adapted from "Quantum effects in biology" Graham R. Fleming, Gregory D. Scholes, Yuan-Chung Cheng. Copyright © 2011 Published by Elsevier B.V.. Used with permission under licence 5156420935296)

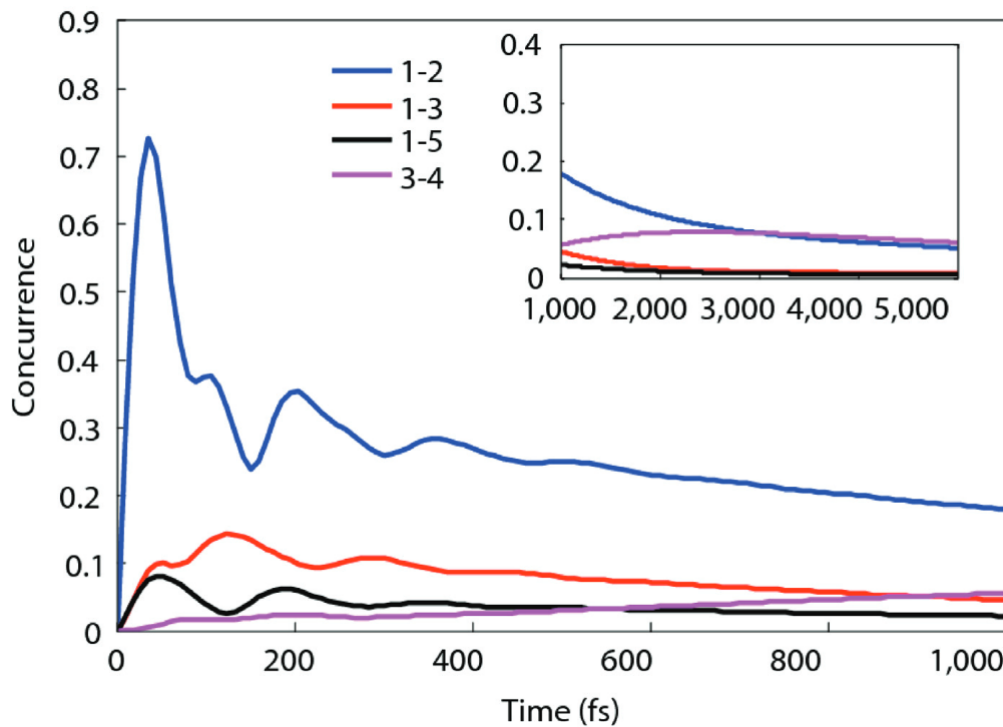


Figure 2.6: Figure shows the coherences between most entangled sites given in Figure 2.5. (Adapted from "Quantum effects in biology" Graham R. Fleming, Gregory D. Scholes, Yuan-Chung Cheng. Copyright © 2011 Published by Elsevier B.V.. Used with permission under licence 5156420935296)

often thought to decay rapidly and therefore commonly neglected during theory formulations. But recent developments in two-dimensional spectroscopy suggest that there are coherences lasting for a time period that can be comparable to RET dynamics. Therefore, these quantum coherences can no longer be neglected in describing photosynthetic process in light harvesting systems.

2.3 Open Quantum Systems

Most studies have modelled quantum systems as a closed system which consists a system of interest (open system) and a surrounding environment (which is also referred to as the bath or heat reservoir). The energy contained in this open

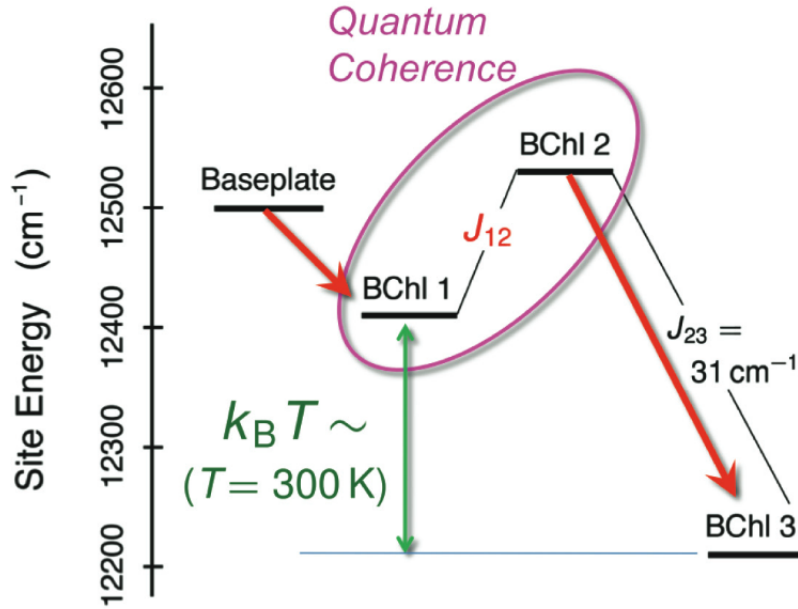


Figure 2.7: Structure of the considered energy transferring path for Figure 2.8. (Adapted from "Quantum effects in biology" Graham R. Fleming, Gregory D. Scholes, Yuan-Chung Cheng. Copyright © 2011 Published by Elsevier B.V.. Used with permission under licence 5156420935296)

system is being dissipated to the surrounding environment through system-bath coupling. For simplicity, the environment is considered to be in thermal equilibrium and large enough to absorb small fluctuations forced by the system. Since, such a closed quantum system has an infinite amount of degrees of freedom, we cannot use unitary transformation methods to identify time evolution of the quantum states. Such non-unitary dynamics could be explored using a quantum master equation derived utilizing the motion of the density matrix of the closed quantum system. Liouville's super operators are used to model this type of time evolution in quantum systems. System density matrix ($\hat{\rho}(t)$) and corresponding quantum Liouville operator ($\hat{\mathcal{L}}$) are related by,

$$\frac{d\hat{\rho}(t)}{dt} = -i\hat{\mathcal{L}}\hat{\rho}(t) = -i[\hat{\rho}(t), \hat{H}] \quad (2.5)$$

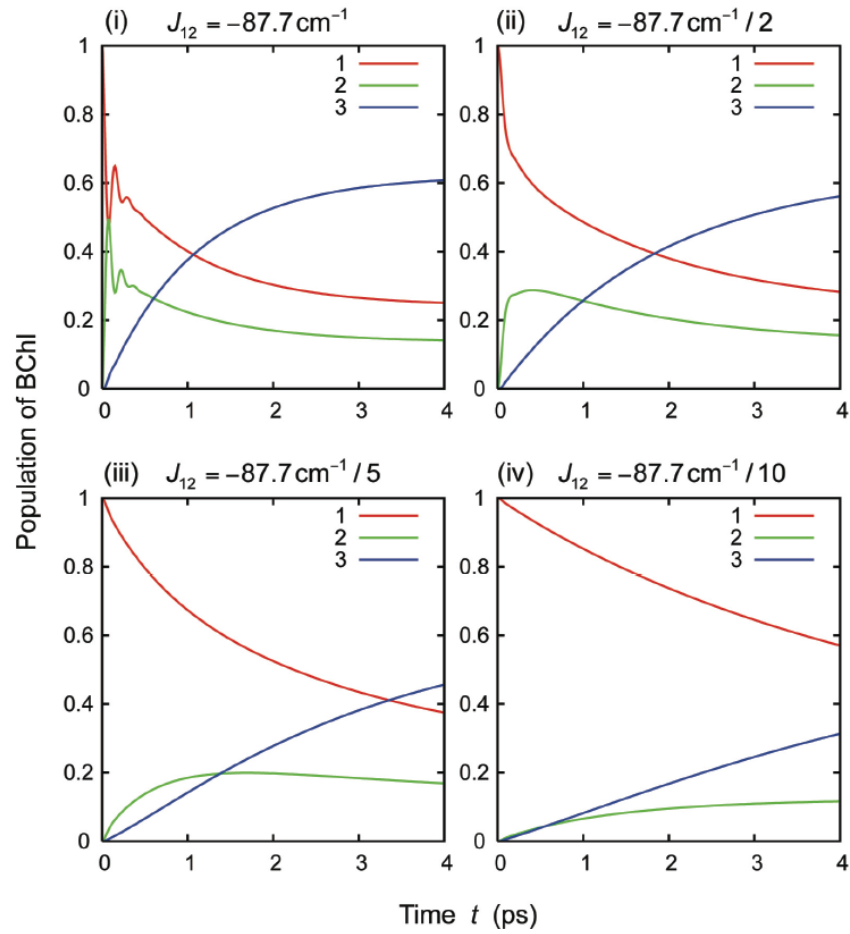


Figure 2.8: Population of each site for different coupling (J_{12}) values. (Adapted from "Quantum effects in biology" Graham R. Fleming, Gregory D. Scholes, Yuan-Chung Cheng. Copyright © 2011 Published by Elsevier B.V.. Used with permission under licence 5156420935296)

where $\hat{H}$ is the Hamiltonian of the quantum system.

Further, since our interest lies on the open quantum system, we could reduce the density matrix to only include open system states in order to derive the quantum master equation [55]. Incorporating this quantum master equation, one can look into the state dynamics and states' evolution with time.

2.3.1 Spin boson model

The two state quantum system is the build block of all quantum systems. Therefore, it is naturally to build theories around these two state systems and spin boson model is the common way of modelling such systems in literature. In this model, the two quantum states are modelled using spins and the environment is represented as a set of bosons or a set of harmonic oscillators.

2.3.2 Markovian assumption

The type of equation we derive to simulate states' evolution, depends on the importance of Markovian dynamics considered for the system. Initially, even though the energy we are interested is confined to the open system (particularly at the donor chromophore), this energy dissipates to other chromophores in the open system as well as to the environment. Such energy flow is influenced by inter-chromophore coupling as well as the coupling of chromophores towards the bath modes of the environment. If this environment is very large and bath correlations among the bath modes are high, the energy transferred to the environment is lost after a time period. When this irreversible dissipation takes place, such an arrangement is considered as a Markovian environment. When the energy backflow from environment to the system is negligible, such an environment is memoryless and one can derive a first-order linear differential equation with the systems states of the density matrix, known as the Lindblad equation [40] to explore the dynamics of the system.

On the contrary, if the environment is comparatively small and there are strong system-bath correlations (governed by the spectral density function of the bath) compared to the bath correlations, such an environment is considered as non-Markovian. Non-Markovian environments support energy backflow from the environment to the system of interest where energy is not destroyed once the dis-

sipation occurs to the bath. Such environments retain memory and dynamics of open systems attached to such environments are extremely complex owing to the degrees of freedom in the bath. By tracing out environmental degrees of freedom from the density matrix, we can derive a quantum master equation to study its dynamics. Furthermore, we can opt to derive a higher order equation but it has been shown that second order quantum master equations can simulate the energy transfer to an acceptable accuracy whereby the accuracy gain of having a higher order equation is minimal, compared to its computational complexity and time complexity [56]. In this study, we are interested in a quantum master equation which could explain non-Markovian dynamics.

Such quantum master equations could be divided into three major categories depending on the relative strength of system bath coupling. If the influence of the environment is strong compared to the interaction between system sites, excitations generated with the energy are localized and the resultant transfer is incoherent, the dynamics of which can be fully analysed by Förster Theory [1,2,6]. On the other hand, a weak system-bath coupling parameter leads to a Redfield type quantum master equation [40] and ensuing energy transfer falls under the coherent regime. When bath influence is comparable to other system parameters, resulting energy transfer characteristics interpolate between coherent and incoherent regimes. For this situation, multiple formalisms based on second-order perturbation theory have been introduced: namely, modified Redfield theory [41,42], full polaron [45,46] transformation-based theory and variational polaron transformation [43,44] based theory. Besides, numerically exact results can also be obtained using non-perturbed methods such as hierarchical equations of motion [47], density matrix re-normalization group [48] and the path integral [49] formalism. However, the latter theories are complex and computationally expensive compared to second-order perturbation theory based formalisms. Further, when we study multisite systems using such numerically exact methods, time

complexity of such calculations usually increases exponentially due to the increased number of degrees of freedom in the open system.

2.4 Polaron Transformation

The polaron theory in condense matter physics describes how a polaron, a quantum (quasi-) particle which is a fundamental building-block, interacts with the deformed lattices through electromagnetic interactions [57]. On the other hand, the polaron transformation method transforms the original frame of a Hamiltonian into polaron frame where the quantum master equation generated through the density matrix, is in the acceptable regime so that second-order perturbation theory can be applied to it. The same way a polaron particle can deform the lattice and alter the strength of chemical bonds, by using this unitary transformation technique we change the coupling of the sites(donor and acceptor) and the environment. Because of this similarity in changing coupling strengths, this unitary transformation is named polaron transformation, but these two are separate concepts. It is important to make it clear that the role of polaron transformation is not to impose actual physical formation of polarons. Rather, it is merely used as a unitary transformation that helps to identify a term of Hamiltonian that remains small beyond conventional weak-system bath coupling regime. Then, a QME truncated at finite orders of this term can serve as an approximation that works well even in the intermediate or strong system-bath coupling limit [46]. In other words, this is essentially a unitary transformation method which alters the interactions between donor and acceptor and between donor/acceptor and the environment.

This transformation can be used to solve spin boson models, since it holds true for a range of coupling strengths, it is clear in physical pictures and can be easily extended to multi state systems [57]. The concept behind polaron trans-

formation method is to convert all quantum system related parameters into the polaron frame such that open quantum system is dressed by the environmental factors. Such conversion changes the site energies into polaron shifted site energies and site interaction strengths to renormalized site coupling strengths. To further discuss this transformation consider the following Hamiltonian of a closed quantum two-state system [45] consists of an excited donor state ($|D\rangle$) and an excited acceptor state ($|A\rangle$),

$$H_T = H_s^p + H_s^c + H_{sb} + H_b \quad (2.6)$$

where,

H_T - Total Hamiltonian

H_s^p - Hamiltonian of the system populations

H_s^c - Hamiltonian of the system coherences

H_{sb} - Hamiltonian of system and bath coupling

H_b - Hamiltonian of the bath

Each of these Hamiltonians can be expanded as follows using the bra-ket notation.

$$H_s^p = E_D |D\rangle \langle D| + E_A |A\rangle \langle A| \quad (2.7)$$

$$H_s^c = J(|A\rangle \langle D| + |D\rangle \langle A|) \quad (2.8)$$

$$H_{sb} = B_D |D\rangle \langle D| + B_A |A\rangle \langle A| \quad (2.9)$$

where,

E_D (E_A) - site energy at $|D\rangle$ ($|A\rangle$)

J - resonance coupling between $|A\rangle$ and $|D\rangle$

B_D (B_A) - bath operator coupled to $|D\rangle$ ($|A\rangle$)

Now consider the following polaron generator function,

$$G = \sum f_n (b_n^\dagger - b_n) (g_{nD} |D\rangle \langle D| + g_{nA} |A\rangle \langle A|) \quad (2.10)$$

which used as the unitary transformation function. Here, g_{nA} (g_{nD}) is defined as the coupling strength of bath's n mode to $|A\rangle$ ($|D\rangle$) state of the TLS, f_n is the variational parameter and $b_n^\dagger$ (b_n) is the n^{th} mode creation (annihilation) operator with frequency ω_n . Now we can perform the polaron transformation by calculating,

$$\tilde{H}_T = e^G H_T e^{-G} \quad (2.11)$$

which transforms the original frame of reference to an alternative frame known as the polaron frame. The polaron generator function (G) displaces the bath oscillators in positive or negative direction depending on the system states. The variational parameter f_n determines the magnitude of this displacement for each bath mode. Therefore, note that the value of f_n is very important which could be in the range of $0 \leq f_n \leq g_n$ and depending on its value we can alter the type of polaron transformation applied to the system. There are essentially three types of polaron transformation available in the literature depending on the value of f_n ,

1. No polaron transformation ($f_n = 0$)
2. Full polaron transformation ($f_n = g_n$)
3. Variational polaron transformation ($0 \leq f_n \leq g_n$).

When we eliminate the variational parameter ($f_n = 0$), this configuration is known as no polaron transformation and in this case quantum master equations are derived using the original frame of reference of the Hamiltonians.

2.4.1 Full polaron transformation

In full polaron transformation method, we displace the bath oscillators attached to a quantum state from the same magnitude that this quantum state is coupled with that bath mode. This form of polaron transformation leads to full polaron based quantum master equations which perform well in super-ohmic environments for fast baths [58]. When it comes to ohmic environments, this quantum master equation undergoes severe distortions due to the infrared divergence effect of bath correlation functions. The bath correlation functions ($\mathcal{K}(t)$) in full polaron transformation based quantum master equations is in the form of,

$$\mathcal{K}(t) = \sum_n (g_{nD} - g_{nA})^2 \{ \coth(\beta \hbar \omega_n / 2) \cos(\omega_n t) - i \sin(\omega_n t) \} \quad (2.12)$$

2.4.2 Variational polaron transformation

When we let the variational parameter (f_k) float between 0 and the system bath coupling strength, that configuration is known as variational polaron transformation method. Unlike in full polaron transformation, we allow the displacement of bath modes coupled to the interested site to achieve a value in the above specified region. Once this transformation takes place, the total system Hamiltonian could be divided into two categories, zeroth order Hamiltonian and the first order Hamiltonian. Calculation of the exact f_k value is achieved by minimizing the contribution of the first order Hamiltonian to the free energy. To minimize the free energy, we use Feynman-Bogoliubov upper bound on the free energy [59] as been shown in [43,44]. Feynman-Bogoliubov upper bound on the free energy is given by,

$$A_{\text{FB}} = -\frac{1}{\beta} \ln \left[\text{Tr} \left\{ e^{-\beta \hat{H}_0} \right\} \right] + \langle \hat{H}_1 \rangle_{\hat{H}_0} + O \left(\langle \hat{H}_1^2 \rangle_{\hat{H}_0} \right). \quad (2.13)$$

An improved version of free energy minimization equation has been introduced in [60] where higher order terms have been also considered. True free energy A is related to A_{FB} through the inequality $A_{\text{FB}} \geq A$ and the second term of the above equation is zero by construction. Therefore, the above equation now stands at,

$$A \leq A_{\text{FB}} = -\frac{1}{\beta} \ln \left[\text{Tr} \left\{ e^{-\beta \hat{H}_0} \right\} \right]. \quad (2.14)$$

when higher order terms are neglected. Following this we could take the derivative of A_{FB} with respect to f_k in order to minimize the free energy which results in two equation which should be solved self consistently. We will demonstrate this process in chapter 4.

According to literature, as a consistent theory valid in all system-bath coupling regimes, which is also relatively simple and computationally inexpensive, variational polaron transformed master equation has performed well in ohmic, sub-ohmic and super-ohmic environments for both fast and slow baths [58]. While full polaron transformation works well in fast super-ohmic baths, it suffers from infrared divergence effect as a consequence of the full polaron approximation.

2.5 Spectral Density Functions

As elucidated earlier, spectral density functions (SDFs) govern how bath modes are attached to the consider quantum system sites. Unsurprisingly, the choice of SDF for modelling a specific EET system is an important component of the model as it essentially dictates the energy exchange dynamics of the donor and the acceptor with the environment (bath). Specifically, SDFs model the energy relaxation dynamics of the donor and the acceptor. In this section, we look at three main categories of spectral density functions,

1. Standard spectral density function

2. Log-normal spectral density function
3. Combined spectral density function with logarithmic perturbations.

2.5.1 Standard spectral density function

Generally, to define the spectral density function (SDF) of a bath attached to a quantum system, we use the well known Ohmic-like spectral density function [43,44,46] given by,

$$J(\omega) = q\omega_c^{1-\alpha}\omega^\alpha e^{-\omega/\omega_c}, \quad (2.15)$$

where q is the dimensionless bath coupling strength, ω_c is the cut-off frequency and α is the Ohmicity parameter. Ohmicity parameter α governs how SDF scales linearly for low frequency bath modes. When $\alpha < 1$, SDF scales sub-linearly and therefore, such an environment is identified as sub-Ohmic. On the other hand, when $\alpha > 1$, SDF scales super-linearly and such an environment is identified as super-Ohmic. In Ohmic environments, SDF scales linearly at low frequencies where $\alpha = 1$ [61].

2.5.2 Log-normal spectral density function

Despite the fact that most quantum environments can be illustrated through above standard spectral density function, recently introduced log-normal type spectral density function given in Eq. (2.16) has shown to be more accurate in replicating spectral density functions obtained through experimental works [52].

$$J(\omega) = q \exp \left\{ -\frac{1}{2\sigma_{SD}^2} \left[\ln \left(\frac{\omega}{\omega_c} \right) \right]^2 \right\} \quad (2.16)$$

This is owing to the presence of two tunable parameters (ω_c and σ_{SD}) which aids in fitting a shape more precisely to an experimental data set. This log-normal

spectral density function also entails logarithmic factors of various powers which are not uncommon in decay dynamics. In fact, it has been shown both experimentally and quantum mechanically that long term relaxation of a quantum system could include inverse power law factors combined with logarithmic corrections [62]. These logarithmic factors are also innate in low frequency power series expansions of spectral density functions.

2.5.3 Combined spectral density function with logarithmic perturbations

In many unstable (excited) physical systems, energy relaxation follows exponential behaviour over time to a very good approximation. However, it has been shown both theoretically and experimentally, that many of the physical systems that are known to exhibit exponential relaxation actually deviates from this behaviour at long time scales [63–68]. In the specific case of energy decay in excited electronic systems, quantum mechanical treatments of unstable atoms have shown that the long term behaviour actually contains both inverse power law ($1/t^2$) as well as logarithmic ($1/t \log^2(t)$) corrections to the exponential decay dynamics [62]. This implies the existence of a component that relaxes much slower at longer time scales than expected. The most widely used types of SDFs for modelling EET systems are the sub-Ohmic, Ohmic and the super-Ohmic spectral densities, and they are widely used to effectively model many real systems [69, 70]. However, these ohmic-like SDFs only exhibit inverse power law behaviour for long-time relaxation rates and hence cannot be expected to faithfully produce physical results for long time scales. In [51, 71], a general class of functions with logarithmic corrections to ohmic-like SDFs have been shown to be able to replicate the inverse logarithmic behaviour at long times, in addition to the inverse power law behaviour. Almost all quantum mechanical investigations of EET performed until now have focused on ohmic-like SDFs and hence have not been sen-

sitive to these logarithmic deviations expected at long time scales. These effects will be significant in any excitation transfer system that relies on exact estimates of long term behaviour of such systems. For example, excitation transfer system designed for energy harvesting, information transfer and a multitude of other applications will need to consider these effects due to the need for accurate estimates of the system on long time scales. Logarithmic relaxation is by no means a new physical phenomenon and similar logarithmic relaxations are also found in wave propagation in solid materials [72], molecular liquids [73], proteins [74,75], visco-elasticity [76] and glass-forming systems [77,78]. In addition to this, in [52] it was shown that SDFs in log-normal form that is similar to the SDFs we use, replicate the experimentally observed results better than the conventional Ohmic, super-Ohmic and sub-Ohmic SDFs.

Incorporating these logarithmic factors an Ohmic-like spectral density function has been introduced and can be expressed as [51],

$$J(\omega) = q\omega_c \left(\frac{\omega}{\omega_c}\right)^\alpha \exp\left(\frac{-l\omega}{\omega_c}\right) \left|\ln\left(\frac{\omega}{\omega_c}\right)\right|^n. \quad (2.17)$$

Above version of Ohmic-like spectral density function has been utilized to exemplify quantum environments which are slightly deviated from the original form. This deviation is obtained through the logarithmic perturbation factor (n) in above equation. Furthermore, this form of spectral density functions are capable of characterizing a large range of relaxations which are slower than the exponential decay and faster or slower than the inverse power laws in quantum systems [51]. Our goal in this thesis is to examine the coherent energy transfer dynamics of quantum systems through polaron transformation based quantum master equations where the attached quantum environments are slightly disturbed/perturbed in the frequency domain which are described through this novel type of spectral density function. In an effort to visualize Eq. (2.17) in the frequency domain, we have plotted Figure. 2.9 where $\omega_c = 3$ THz, $l=1.1$, $q=0.005$

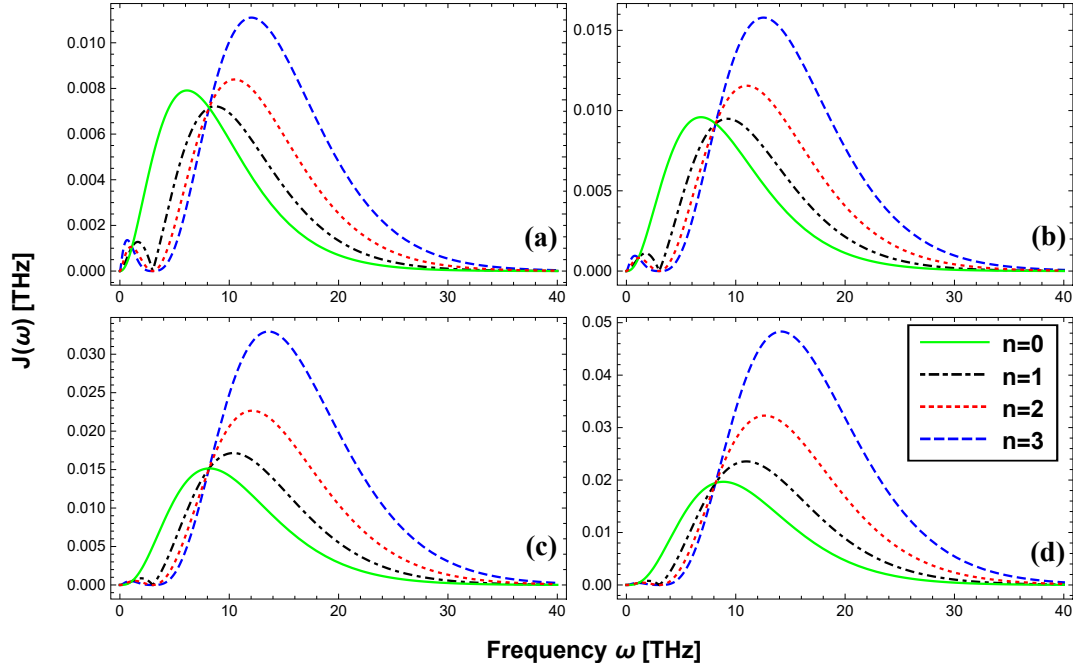


Figure 2.9: Spectral density functions of $J(\omega)$ for the values of (a) $\alpha=2.25$, (b) $\alpha=2.5$, (c) $\alpha=3$, (d) $\alpha=3.25$. Values of n are shown on the graphs. For each case we take $\omega_c = 3$ THz, $l=1.1$ and $q=0.005$.

and (a) $\alpha=2.25$, (b) $\alpha=2.5$, (c) $\alpha=3$, (d) $\alpha=3.25$. We can delineate the fact that for all α and n values, $J_{\alpha,n}$ graphs intersect at $\omega = \omega_c/e$ and at $\omega = \omega_c e$. Thus, we observe three distinct frequency regions for each Ohmicity value (α).

- The low-frequency range $(0, \omega_c/e)$, in which $J_{\alpha,n_1} < J_{\alpha,n_2}$ for all $n_1 < n_2$.
- The intermediate range $(\omega_c/e, \omega_c e)$, in which $J_{\alpha,n_1} < J_{\alpha,n_2}$ for all $n_1 > n_2$.
- The high-frequency range $(\omega_c e, \infty)$, in which $J_{\alpha,n_1} < J_{\alpha,n_2}$ for all $n_1 < n_2$.

It can be clearly observed the fact that logarithmic perturbation factors have alter the low-frequency dynamics in each graph. As we increment the α value, the contribution from low-frequency range frequency modes to the overall coupling strength is apparently reduced. In the intermediate frequency range, we see that smaller logarithmic perturbation factors correspond to the larger coupling strengths. It is also important to note that, when these logarithmic factors are present, bath coupling strength near the cut-off frequency becomes neg-

ligible with a removable logarithmic singularity. Finally, in the high-frequency range, we see that larger n values correspond to larger total system-bath coupling strengths when comparing the area under the curves.

2.6 RET Based Applications

Applications based on RET are broad which include artificial light harvesting devices, molecular biology, spasers, quantum computation etc. As previously elucidated, the highly efficient nature of the RET inspired many novel applications such as two-dimensional spectroscopy and imaging microscopy. Therefore, in this section, an overview of RET based applications will be discussed.

2.6.1 Solar cells

Photosynthesis phenomena has influenced researchers and scientist to use a similar mechanism to convert solar energy to electricity, which has become a prime area of research over last few decades. Artificial light harvesting devices such as organic solar cells have become popular due to their flexibility, miniature structure and being lightweight compared to other options [79,80]. Current organic solar cells could reach beyond ten percent power conversion efficiency. This benchmark will be increased over the next decade especially with the technological advancements of the manufacturing industry.

The procedure of solar energy conversion could be divided into 5 main stages: solar light absorption, transportation of generated excitons, exciton dissociation, charge transportation, and charge separation. While the latter two stages are not directly involved with RET mechanism, the first three stages are highly relevant. Particularly in exciton transport stage, diffusion processes take control and transport excitons from regions where the exciton concentration is high. Since, inter

molecular interactions are low compared to other environmental interactions, in most organic solar cells this transport occurs as a hopping mechanism. If parameters related to this hopping mechanism discourage the exciton transport, electron-hole pairs will recombine and the absorbed energy will be lost after this event.

Further, exciton dissociation which separates the generated electron from the electron-hole pair plays a major role in this mechanism. As electrons are moving from donor to the acceptor, holes are moving from acceptor to the donor. During this exciton dissociation influenced by chemical potential difference, impurities also tends to involve in the process which leads to trapped excitons in energy barriers. Such events are counter-productive where we focus on the device performance. In terms of solar energy harvesting stage, solar concentrators are utilized to generate a higher quantum yield which uses FRET mechanism.

It has been shown that polymer solar cells which are based on FEET theory, gained a 38 percent increase in power conversion efficiency when mixed with a squaraine dye. The reason for this increased efficiency is due to the additional energy migration occurred from one molecule to another over long spatial distances. The squaraine dye is extremely absorbent in the infrared region which expands the spectral absorption of these solar cells while enhancing the transmission of generated electricity [81].

2.6.2 Distance measurements

Being a high distance dependent energy transfer scheme, FRET has been used to measure nanometre distances [82]. Most common distant measurement based on FRET theory is to measure distances between two molecules. FRET based applications are more sensitive than other methods that has been utilized for this purpose. In addition, high temporal resolution and low spatial resolution

of FRET has made it possible to do measurements in complex systems such as plasma membrane of intact cells [83]. Fluorochromes are placed at several points in system under measurement with the help of flexible linkers. Using FRET theory, angstrom level of accuracy and precision could be measured based on the efficiency received at acceptor molecules [84].

2.6.3 Biosensors

Another FRET based application which is commonly used in cellular molecular dynamics, cell-cell interactions and cellular physiology is biosensors. Such biosensors based on FRET mechanism are made of a donor, an acceptor, a sensor domain, a ligand and linkers. Biosensors could be largely divided into two categories namely intermolecular biosensors (bimolecular) and intramolecular biosensors (unimolecular) where intramolecular biosensors could be further categorized into distance change-based and fluorescence property change-based biosensors.

This categorization is based on how FRET ratio is changed when detected by a chemical signal. The distance change-based FRET biosensors can be further divided into 3 types: cleavage-based, mechanical force-based and conformational change-based. Contemporary experiments that utilized FRET based biosensors include determining potency of cancer drugs [85], necroptosis [86], autophagy [87], dynamic Lck activation in T cells [88], Visualizing Cell-Environment Interaction [89], breast cancer cells [90,91].

Furthermore, FRET based biosensors are successfully applied in intracellular mechanotransduction which studies the mechanotransduction process occurs due to cellular responses stem from the conversion of biomechanical signals into biochemical signals.

2.6.4 Optical Microscopy

To investigate a certain system such as a protein through microscopy, a donor and acceptor are attached to these systems. These pairs should have characteristics of a donor acceptor pair that can involve with FRET mechanism such as, Alexa488–Cy3, BFP–GFP, BFP–Red Fluorescent Protein RFP, Cyan Fluorescent Protein CFP–YFP, Cy3–Cy5, CFP–RFP, FITC–Rhodamine and BFP–YFP [92, 93]. There are multiple ways of measuring the FRET in microscopy namely; Acceptor photobleaching, Sensitized emission, Fluorescence-lifetime imaging microscopy (FLIM)-FRET and Polarized anisotropy. There are advantages and disadvantages of using these measuring schemes, for example, a few major advantages of using FLIM based measurements is that it requires only a donor FP to get measurements, it is less bothered by photobleaching and it does not get affected if the protein concentration is low in general. But there are disadvantages such as being a slow measurement process, being very expensive which requires specialized equipment to measure time and frequency domain data and may need complex analysis of data gathered, during quantitation. In general, the lifetime of the fluorescence is dependent on environmental factors such as the refractive index of the medium, pH level and ion concentration of the sample.

2.7 Summary

In summary, there are two major categories in energy transfer mechanisms between molecules, radiative and non-radiative energy transfer. Non-radiative energy transfer is possible in two forms, Dexter Resonance Energy Transfer (DRET) and Förster Resonance Energy Transfer (FRET). Being a core constituent of quantum physics and nano-photonics, the resonance energy transfer process takes place in photosynthesis has brought forth prime research interest owing to its highly efficient nature. Parameters in both the quantum system and the sur-

rounding environment (bath) strictly regulate this crucial energy transfer process. While spectral density function (SDF) governs the environmental influence, multiple theories have been instituted to delineate diverse aspects of the said transfer.

Förster Theory introduced in 1948, assumes that coupling between quantum sites and environment is significant compared to other parameters of the quantum system. Thus, it exemplifies an energy transfer transpires in the incoherent regime. On the contrary, Redfield or Lindblad theory elucidates an energy transfer in a quantum system where the coupling between the environment and quantum sites is negligible. Whereas, when the environmental influence to the quantum sites can be comparable to other parameters, we identify that the quantum system is in the intermediate coupling regime. Recent developments in two-dimensional spectroscopy have discovered some light harvesting systems such as Fenna Matthews Olson complex, works in the intermediate coupling regime where inter-molecule coupling is comparable to the system bath coupling. Theories applicable in this regime can be divided into two major categories: numerically exact methods such as hierarchical equations of motion, density matrix renormalization group, path integral formalism, and second-order perturbation methods such as modified Redfield theory, variational polaron transformation based theory and full polaron transformation-based theory. Even though numerically exact methods determine the energy transfer more accurately, second-order based methods are computationally less expensive with an acceptable accuracy.

In most instances found in literature, the energy transfer process is studied against the most common type of Ohmic-like SDFs consisting of n exponential decay term, where the type of the environment (whether it is sub-Ohmic, Ohmic, or super-Ohmic) is determined by the Ohmicity parameter [43–45, 69, 70]. Even though, majority of relevant quantum systems can be portrayed through these common types of SDFs, recently introduced log-normal type SDF [52] is capable of mimicking experimental data more precisely. This log-normal type SDF

uses logarithmic factors of various power magnitudes to construct an accurate SDF, and these logarithmic factors are not used in an arbitrary context. They are present in the low frequency power series expansion of the SDF [51]. Accounting for these logarithmic factors, a SDF has been developed recently to incorporate the slow relaxation term over a long time scale, which occur in many systems [62–68]. By influencing slight perturbations in the frequency domain through these logarithmic factors, this SDF attempts to formulate an environment that is slightly different from the common Ohmic-like SDFs.

Chapter 3

Energy transport in a disturbed environment utilizing two-level full polaron transformation approach

3.1 Introduction

In this chapter, we intend to analyse energy transfer dynamics of a pair of interacting chromophores immersed in a disrupted quantum environment as shown in Figure 3.1. Evolution of energy of a two-level donor-acceptor pair has gained traction in recent years as elucidated in chapter 2. While contemporary research has studied this evolution in various quantum environments, we analyse the energy transfer dynamics when the attached quantum environment is disturbed from the standard sub-ohmic, ohmic and super-ohmic categorization. As described in chapter 2, we utilize a general SDF which could be used to simulate these disturbances for the study.

The donor-acceptor pair considered in this chapter, is assumed to have a significance coupling among them compared to their coupling with the environment. Since, Förster theory is not suitable for such systems, we incorporated the full-polaron transformation method to formalize the quantum master equation. Full-polaron based quantum master equation is popular when studying super-ohmic environments due to the accuracy of the generated results, specially in fast

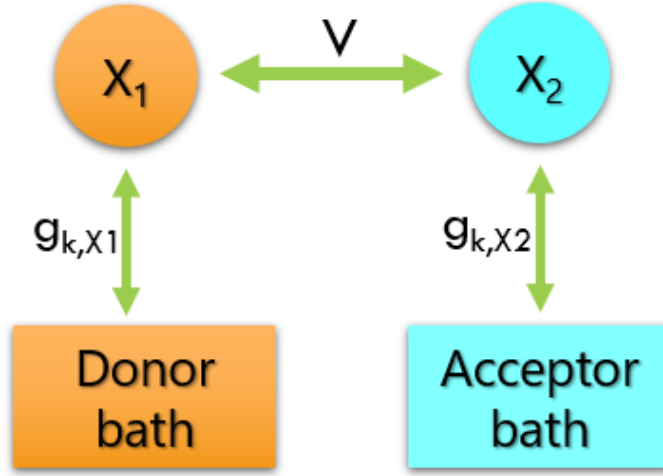


Figure 3.1: Donor chromophore (X_1) and an acceptor chromophore (X_2) are connected to identical and independent baths. V represents the inter-chromophore coupling whereas $g_{k,X1}$ ($g_{k,X2}$) represents the coupling between k^{th} bath mode and X_1 (X_2) site.

baths. Our purpose in this chapter would be to gauge the performance of this quantum master equation in disturbed quantum super-ohmic environments. In addition, we are also interested in the simulated dynamics in such environments.

This chapter is outlined as below. Following the introduction, in section 3.2, the formalism including the model and the analytical approach deployed for our analysis is outlined. In section 3.3, the results obtained for super-Ohmic SDFs with logarithmic perturbations are discussed. Finally, section 3.4 summarizes and concludes the chapter.

3.2 Formalism

Let's consider a spin boson model [43–45, 60] that consists of a donor (X_1) chromophore, an acceptor (X_2) chromophore and an encompassing boson environment. At the start of the study (at $t=0$), total system including the environment and all other degrees of freedom are in thermal equilibrium in ground state denoted by $|G\rangle$. Let's model $|X_j\rangle$ as the state where X_j site is excited and the re-

maining site to be in ground state ($j = 1, 2$). As this study is interested only in the single excitation state space, the three states which entirely elucidate the system are $|X_1\rangle, |X_2\rangle$ and $|G\rangle$.

To start with the study, let's excite the donor molecule to state $|X_1\rangle$ using a laser pulse. Laser pulse has a duration of τ_{laser} and this quantity should be much smaller than the spontaneous decay time τ_{sd} ($\tau_{laser} \ll \tau_{sd}$) to the ground. Under these circumstances, initial condition of the complete system can be written as,

$$\hat{\rho}(0) = \hat{\rho}_S(0) \otimes \frac{e^{-\beta \hat{H}'_b}}{Z}, \quad (3.1)$$

where the partition function is denoted by $Z = \text{Tr}_b\{e^{-\beta \hat{H}'_b}\}$ which is the trace over the bath degrees of freedom. Here, system Hamiltonian can be written as $\hat{\rho}_S(0) = |X_1\rangle \langle X_1|$ since the entire population is at $|X_1\rangle$ initially and $\beta = 1/k_B T$ where k_B is the Boltzmann's constant and T is the temperature of the system in Kelvins.

3.2.1 Hamiltonian of the total system

First we define the Pauli operators,

$$\begin{aligned} \hat{\sigma}_z &= |X_1\rangle \langle X_1| - |X_2\rangle \langle X_2| \\ \hat{\sigma}_y &= i(|X_2\rangle \langle X_1| - |X_1\rangle \langle X_2|) \\ \hat{\sigma}_x &= |X_1\rangle \langle X_2| + |X_2\rangle \langle X_1|. \end{aligned}$$

The total Hamiltonian of the complete system can be written as,

$$\hat{H}' = \hat{H}'_p + \hat{H}'_c + \hat{H}'_{sb} + \hat{H}'_b, \quad (3.2)$$

where, $\hat{H}'_p = (\epsilon/2)\hat{\sigma}_z$ is the population Hamiltonian that represents the energy localized at each chromophore. Here, $\epsilon = \epsilon_1 - \epsilon_2$ represents the energy difference

between the states $|X_1\rangle$ and $|X_2\rangle$. The energy de-localized between the two chromophores are given by the Hamiltonian of the coherences denoted by $\hat{H}'_c = V\hat{\sigma}_x$, where V is the electronic coupling strength between the donor-acceptor pair. Hamiltonian of the system-bath coupling is given by,

$$\hat{H}'_{sb} = \sum_{j=1,2} |X_j\rangle \langle X_j| \sum_k \hbar\omega_{k,j} g_{k,j} (\hat{b}_{k,j}^\dagger + \hat{b}_{k,j}) \quad (3.3)$$

where $b_{k,j}^\dagger (b_{k,j})$ is the k^{th} bath mode creation (annihilation) operator with frequency $\omega_{k,j}$ attached to the site X_j ($j = 1, 2$) and the system-bath coupling between k^{th} mode and X_j^{th} site is denoted by $g_{k,j}$. The system-bath coupling denoted by $g_{k,j}$ is for k^{th} bath attached to j^{th} site, which is fully described through the bath SDF $J(\omega)$ for a spin boson model [43–45,60] which we elucidate later in Sec. 3.2.4. Bath Hamiltonian is given by $\hat{H}'_b = \sum_{j=1,2} \sum_k \hbar\omega_{k,j} b_{k,j}^\dagger b_{k,j}$. Now we can write the expanded form of the total system Hamiltonian as,

$$\hat{H}' = (\epsilon/2)\hat{\sigma}_z + V\hat{\sigma}_x + \sum_{j=1,2} |X_j\rangle \langle X_j| \sum_k \hbar\omega_{k,j} g_{k,j} (\hat{b}_{k,j}^\dagger + \hat{b}_{k,j}) + \sum_{j=1,2} \sum_k \hbar\omega_{k,j} b_{k,j}^\dagger b_{k,j}. \quad (3.4)$$

Now, let's assume that baths attached to both chromophores are identical and independent. Then the above expression for total system Hamiltonian simplifies to,

$$\hat{H}' = (\epsilon/2)\hat{\sigma}_z + V\hat{\sigma}_x + \sum_{j=1,2} |X_j\rangle \langle X_j| \sum_k \hbar\omega_k g_k (\hat{b}_k^\dagger + \hat{b}_k) + 2 \sum_k \hbar\omega_k b_k^\dagger b_k. \quad (3.5)$$

Next we define the density matrix for the complete system described above as,

$$\frac{d\hat{\rho}'}{dt} = -i\hat{\mathcal{L}}'\rho(t) = -\frac{i}{\hbar}\{\hat{\rho}', \hat{H}'\}, \quad (3.6)$$

where $\hat{\mathcal{L}}'$ is the quantum Liouville operator corresponding to the total system Hamiltonian $\hat{H}'$. Quantum Liouville operators corresponding to above Hamilto-

nians $\hat{H}'_p, \hat{H}'_c, \hat{H}'_{sb}, \hat{H}'_b$ can be written as $\hat{\mathcal{L}}'_p, \hat{\mathcal{L}}'_c, \hat{\mathcal{L}}'_{sb}$ and $\hat{\mathcal{L}}'_b$. Now we can expand above equation as follows,

$$\frac{d\hat{\rho}'}{dt} = -i(\hat{\mathcal{L}}'_p + \hat{\mathcal{L}}'_c + \hat{\mathcal{L}}'_{sb} + \hat{\mathcal{L}}'_b)\hat{\rho}'(t). \quad (3.7)$$

3.2.2 Full polaron transformation

Now, we use polaron transformation method to convert system Hamiltonians, density matrices and quantum Liouville operators into the polaron frame as shown in [43–45, 55, 58]. Consider the following polaron generator function,

$$G = \sum_{j=1,2} |X_j\rangle \langle X_j| \sum_k \frac{g_k}{\hbar\omega_k} (\hat{b}_k^\dagger - \hat{b}_k). \quad (3.8)$$

We now follow $\hat{H} = e^G \hat{H}' e^{-G}$ to apply full polaron transformation to each Hamiltonian using the polaron generator function given in above. After applying into population Hamiltonian using $\hat{H}_p = e^G \hat{H}'_p e^{-G}$ we obtain,

$$\hat{H}_p = \hat{H}'_p = \frac{\epsilon}{2} \hat{\sigma}_z, \quad (3.9)$$

since $\hat{H}'_p$ is independent of $\hat{b}_{k,j}$ and $\hat{b}_{k,j}^\dagger$. Next we apply the transformation to coherence Hamiltonian given by $\hat{H}_c = e^G \hat{H}'_c e^{-G}$. After using Baker–Campbell–Hausdorff formula to simplify the expression we obtain,

$$\hat{H}_c = V |X_1\rangle \langle X_2| \exp\left(\frac{g_k}{\hbar\omega_k} (\hat{b}_k^\dagger - \hat{b}_k)\right) + V |X_2\rangle \langle X_1| \exp\left(\frac{g_k}{\hbar\omega_k} (\hat{b}_k^\dagger - \hat{b}_k)\right) \quad (3.10)$$

This can be rewritten using bath displacement operators as,

$$\begin{aligned} \hat{H}_c = & VB(|X_1\rangle \langle X_2| + |X_2\rangle \langle X_1|) + V |X_1\rangle \langle X_2| \hat{B}_+ + V |X_2\rangle \langle X_1| \hat{B}_- \\ & - VB(|X_1\rangle \langle X_2| + |X_2\rangle \langle X_1|) \end{aligned}$$

and simplifying it further we reach,

$$\hat{H}_c = V_R \hat{\sigma}_x + \frac{V}{2} [\hat{\sigma}_x (\hat{B}_- + \hat{B}_+ - 2B) + i\hat{\sigma}_y (\hat{B}_+ - \hat{B}_-)] . \quad (3.11)$$

Next we transform the bath Hamiltonian using $\hat{H}_b = e^G \hat{H}'_b e^{-G}$ where we reach,

$$\begin{aligned} \hat{H}_b = \hat{H}'_b + 2 \sum_k \frac{g_k^2}{\hbar\omega_k} - |X_1\rangle \langle X_1| \sum_k \hbar\omega_k g_k (\hat{b}_k^+ + \hat{b}_k) \\ - |X_2\rangle \langle X_2| \sum_k \hbar\omega_k g_k (\hat{b}_k^+ + \hat{b}_k) \end{aligned} \quad (3.12)$$

after simplifying using the Baker–Campbell–Hausdorff formula. Finally, we transform the system-bath Hamiltonian using $\hat{H}_{sb} = e^G \hat{H}'_{sb} e^{-G}$,

$$\begin{aligned} \hat{H}_{sb} = \sum_{j=X_1, X_2} |j\rangle \langle j| \sum_k \hbar\omega_k g_k (\hat{b}_k^+ + \hat{b}_k) - 2 |X_1\rangle \langle X_1| \sum_k \frac{g_k^2}{\hbar\omega_k} \\ - 2 |X_2\rangle \langle X_2| \sum_k \frac{g_k^2}{\hbar\omega_k}. \end{aligned} \quad (3.13)$$

Since the total transformed Hamiltonian is given by $\hat{H} = \hat{H}_p + \hat{H}_c + \hat{H}_b + \hat{H}_{sb}$, it can be expressed as,

$$\hat{H} = \frac{\epsilon}{2} \hat{\sigma}_z + V_R \hat{\sigma}_x + \hat{H}'_b + R\mathbb{1} + \frac{V}{2} [\hat{\sigma}_x (\hat{B}_- + \hat{B}_+ - 2B) + i\hat{\sigma}_y (\hat{B}_+ - \hat{B}_-)] , \quad (3.14)$$

using above simplifications. Now, we can rewrite the above equation in the form of $\hat{H} = \hat{H}_0 + \hat{H}_1$. The zeroth order Hamiltonian is given by,

$$\hat{H}_0 = \frac{\epsilon}{2} \hat{\sigma}_z + V_R \hat{\sigma}_x + \hat{H}'_b + R\mathbb{1} , \quad (3.15)$$

where the term V_R is the renormalized system bath interaction strength which is given by $V_R = VB$ where,

$$B = \exp \left[- \sum_k \frac{g_k^2}{\hbar^2 \omega_k^2} \coth \left(\frac{\hbar \beta \omega_k}{2} \right) \right]. \quad (3.16)$$

Polaron shifted site energy is given by $R = - \sum_k g_k^2 (\hbar \omega_k)^{-1}$ and $\mathbb{1}$ represents the 2x2 identity matrix. First order Hamiltonian is given by

$$\hat{H}_1 = \frac{V}{2} [\hat{\sigma}_x (\hat{B}_- + \hat{B}_+ - 2B) + i\hat{\sigma}_y (\hat{B}_+ - \hat{B}_-)] , \quad (3.17)$$

where $\hat{B}_\pm = \hat{B}'_\pm \hat{B}'_\mp$ are the bath displacement operators are given by

$$\hat{B}'_\pm = \exp \left[\pm \sum_k \frac{g_k}{\hbar \omega_k} (\hat{b}_k^\dagger - \hat{b}_k) \right]. \quad (3.18)$$

First order Hamiltonian is necessary to be small in both weak and strong coupling regimes to construct a QME that can be suitable for both regimes. When exploring Eq. (3.17), it is evident that $\hat{H}_1$ remains small when g_k is small in weak system bath coupling limit and when V remains small in weak site coupling limit. Therefore, we can assure the smallness of $\hat{H}_1$ unless V is very large compared to other parameters, which is generally not the case.

3.2.3 Derivation of full polaron QME

Now we transform the system density matrix into the polaron transformed frame as $\hat{\rho}(t) = e^G \hat{\rho}'(t) e^{-G}$ which yields,

$$\frac{d\hat{\rho}}{dt} = -i (\hat{\mathcal{L}}_s^p + \hat{\mathcal{L}}_s^c + \mathcal{L}_b) \hat{\rho}(t), \quad (3.19)$$

in the expanded form. Further, initial condition of the complete system needs to be transformed as,

$$\hat{\rho}(0) = \sigma(0) \otimes \left(\frac{\hat{B}'_+ e^{-\beta \hat{H}_b} \hat{B}'_-}{Z} \right). \quad (3.20)$$

Until now, all equations are in Schrödinger picture and it is useful to change into the interaction (Dirac) picture of $\hat{H}_0$ to apply the perturbation theory. In the interaction picture of $\hat{H}_0$ we find,

$$\hat{\rho}_I(t) = e^{i\hat{\mathcal{L}}_0(t)t} \hat{\rho}(t), \quad (3.21)$$

where the density matrix in the interaction picture is given by $\hat{\rho}_I(t)$ and the quantum Liouville operator associated to zeroth order Hamiltonian $\hat{H}_0$ $\hat{\mathcal{L}}_0$ is given by $\hat{H}_0$. By differentiating above equation we find,

$$\frac{d\hat{\rho}_I(t)}{dt} = -i [\hat{\rho}_I(t), \hat{H}_{1,I}(t)] = -i\hat{\mathcal{L}}_{1,I}(t)\hat{\rho}_I(t). \quad (3.22)$$

Let's define $\hat{\mathcal{L}}_{1,I}$ as the Liouville operator related to $\hat{H}_{1,I}(t)$ where,

$$\hat{H}_{1,I}(t) = e^{i\hat{H}_0 t} \hat{H}_1 e^{-i\hat{H}_0 t}, \quad (3.23)$$

is the interaction picture first order interaction Hamiltonian. We extract the system component using standard projection operator method [55] defined by $\mathcal{P}(\cdot) \equiv \hat{\rho}_b \text{Tr}_b\{\cdot\}$ and the complimentary projection $\mathcal{Q}(\cdot) = (I - \mathcal{P})(\cdot)$ extracts the irrelevant part of the density matrix. We apply projection operator to Eq. (3.22) and we get,

$$\frac{d\hat{\rho}_I(t)}{dt} = -i\mathcal{P}\hat{\mathcal{L}}_{1,I}(t) \left(\hat{\rho}_I(0) - i \int_0^t \hat{\mathcal{L}}_{1,I}(\tau) \hat{\rho}_I(\tau) d\tau \right). \quad (3.24)$$

Here, we take $\mathcal{P}\hat{\mathcal{L}}_{1,I}(t)\mathcal{P}\hat{\rho}_I(0) = 0$ since $\hat{H}_0$ and $\hat{H}_b$ commutes with each other. Also according to Eq. (3.21) we find $\mathcal{Q}\hat{\rho}_I(0) = \mathcal{Q}\hat{\rho}(0)$. Then Eq. (3.24) simplifies

to,

$$\mathcal{P} \frac{d\hat{\rho}_I(t)}{dt} = -i\mathcal{P}\hat{\mathcal{L}}_{1,I}(t)\mathcal{Q}\hat{\rho}_I(0) - \int_0^t \mathcal{P}\hat{\mathcal{L}}_{1,I}(t)\hat{\mathcal{L}}_{1,I}(\tau) (\mathcal{P}\hat{\rho}_I(\tau) + \mathcal{Q}\hat{\rho}(0)) d\tau. \quad (3.25)$$

For $\hat{\mathcal{L}}_{1,I}(t)$ we have made second-order approximation without substituting further for $\hat{\rho}_I(\tau)$ in Eq. (3.24). The reduced density matrix is defined as, $\hat{\sigma}_I(t) = \text{Tr}_b\{\hat{\rho}_I(t)\} = \mathcal{P}\hat{\rho}_I(t)$ which turns Eq. (3.25) into,

$$\frac{d\hat{\sigma}_I(t)}{dt} = \hat{\mathcal{I}}(t) - \hat{\mathcal{R}}(t)\hat{\sigma}_I(t), \quad (3.26)$$

where,

$$\hat{\mathcal{R}}(t) = \int_0^t \text{Tr}_b \hat{\mathcal{L}}_{1,I}(t)\hat{\mathcal{L}}_{1,I}(\tau)\hat{\rho}_b d\tau, \quad (3.27)$$

is the system component (homogeneous term) and,

$$\hat{\mathcal{I}}(t) = -i \text{Tr}_b \hat{\mathcal{L}}_{1,I}(t)\mathcal{Q}\hat{\rho}(0) - \int_0^t \text{Tr}_b \hat{\mathcal{L}}_{1,I}(t)\mathcal{Q}\hat{\mathcal{L}}_{1,I}(\tau)\hat{\rho}(0)d\tau, \quad (3.28)$$

is the initial state dependent inhomogeneous term. Since this term is dependent on $\mathcal{Q}\hat{\rho}(0)$ (state of the irrelevant part at $t=0$ ps), if we carefully select an initial time when,

$$\frac{\hat{B}'_+ e^{-\beta H_b} \hat{B}'_-}{Z} \approx \frac{e^{-\beta H_b}}{Z}, \quad (3.29)$$

we can ignore the contribution of the inhomogeneous term, which we have assumed in this analysis. Next, we decompose the first order Hamiltonian using both system operators and bath operators as,

$$\hat{H}_1 = \hat{\sigma}_x \otimes V (\hat{B}_- + \hat{B}_+ - 2B) + \hat{\sigma}_y \otimes V (\hat{B}_+ - \hat{B}_-). \quad (3.30)$$

Using the definition of quantum Liouville operators we can simplify Eq. (3.26) and obtain the following form for the homogeneous system component of the

QME in the Schrödinger picture,

$$\begin{aligned} \hat{\mathcal{R}}(t)\hat{\sigma}(t) = & i [\hat{H}_S, \hat{\sigma}(t)] + \frac{1}{2} \sum_{i,j} \sum_{\omega} \mathcal{Y}_{ij}(\omega, t) \left[\hat{A}_i, \hat{\Delta}_{j,\omega} \hat{\sigma}(t) - \hat{\sigma}(t) \hat{\Delta}_{j,\omega}^\dagger \right] \\ & + i \sum_{i,j} \sum_{\omega} \mathcal{S}_{ij}(\omega, t) \left[\hat{A}_i, \hat{\Delta}_{j,\omega} \hat{\sigma}(t) + \hat{\sigma}(t) \hat{\Delta}_{j,\omega}^\dagger \right], \end{aligned} \quad (3.31)$$

where we define, $\mathcal{Y}_{ij} = 2\text{Re}[K_{ij}(\omega, t)]$ and $\mathcal{S}_{ij} = \text{Im}[K_{ij}(\omega, t)]$ with

$$K_{ij}(\omega, t) = \int_0^t d\tau \Lambda_{ij}(\tau) e^{i\hbar\omega\tau}. \quad (3.32)$$

Here $\Lambda_{ij}(\tau)$ are the bath correlation functions which can be calculated using $\Lambda_{ij}(\tau) = \text{Tr}_B\{\hat{B}_{i,I}(\tau)\hat{B}_{j,I}(0)\hat{\rho}_R\}$. Terms $\hat{B}_{i,I}$ and $\hat{B}_{j,I}$ are bath operators in the interaction picture. Bath correlation functions other than $\Lambda_{11}(\tau)$ and $\Lambda_{22}(\tau)$ vanish due to the full polaron limit. We find,

$$\Lambda_{11}(\tau) = \frac{V_R^2}{2} \left(e^{\Phi(\tau)} + e^{-\Phi(\tau)} - 2 \right), \quad (3.33)$$

and,

$$\Lambda_{22}(\tau) = \frac{V_R^2}{2} \left(e^{\Phi(\tau)} - e^{-\Phi(\tau)} \right), \quad (3.34)$$

where,

$$\Phi(\tau) = 2 \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} \left(\cos(\hbar\omega\tau) \coth\left(\frac{\hbar\beta\omega}{2}\right) - i \sin(\hbar\omega\tau) \right). \quad (3.35)$$

Furthermore, in Eq. (3.31) $\hat{H}_S$ represents the Hamiltonian of the reduced density matrix in the Schrödinger picture. The eigenvectors and eigenoperators of $\hat{H}_S$ can be found as $\hat{H}_S |\pm\rangle = (1/2)(2R \pm \eta) |\pm\rangle$ where $\eta = \sqrt{\epsilon^2 + 4V_R^2}$. Terms $\hat{\Delta}_{j,\omega}$ in Eq. (3.31) can be found by decomposing system operators $\hat{A}_i$ as follows,

$$\hat{\Delta}_{i,\omega} = \sum_{E'-E=\omega} |E\rangle \langle E| \hat{A}_i |E'\rangle \langle E'|, \quad (3.36)$$

where $\hat{A}_i = \sum_{\omega} \hat{\Delta}_{i,\omega}$ identity is true. Here $\omega = 0, \pm\eta$ where terms $\hat{\Delta}_{i,\omega}$ takes the summation of all eigenvalues of $\hat{H}_S$ with a fixed energy difference of ω . Eigenoperators of the decomposed system operators in Eq. (3.36) are given by,

$$\hat{\Delta}_{1,\eta} = \cos 2\theta |-\rangle \langle +| , \quad (3.37)$$

$$\hat{\Delta}_{1,0} = \sin 2\theta (|+\rangle \langle +| - |-\rangle \langle -|) , \quad (3.38)$$

$$\hat{\Delta}_{2,\eta} = i |-\rangle \langle +| , \quad (3.39)$$

$$\hat{\Delta}_{2,0} = 0 , \quad (3.40)$$

where $\theta = (1/2) \arctan(2V_R/\epsilon)$. Also for all cases $\hat{\Delta}_{i,-\eta} = \hat{\Delta}_{i,\eta}^\dagger$ identity is true.

3.2.4 Ohmic-like logarithmic spectral density function

Our objective in this chapter is to study the dynamics of an energy transfer where the donor-acceptor pair is attached to a slightly disturbed super-Ohmic environment. To model this disturbance or slight perturbations, we use the logarithmic terms present in the low frequency power series expansion to perturb the most common type of SDF present in the literature. The reason for using these logarithmic terms to perturb the SDF is due to the physical differences between the exponential decay and the logarithmic decay. To incorporate these logarithmic terms, following form of the SDF has been introduced recently (see figure description of Fig. 1 [51]),

$$J(\omega) = q\omega_c \left(\frac{\omega}{\omega_c}\right)^\alpha \exp\left(\frac{-l\omega}{\omega_c}\right) \left|\ln\left(\frac{\omega}{\omega_c}\right)\right|^n , \quad (3.41)$$

where l represents the scale of the exponential decay, n is the order of logarithmic perturbation in the SDF, ω_c is the cut-off frequency and q is the dimensionless bath coupling strength [43–46, 58] (refer Figure 3.2). Ohmicity parameter α gov-

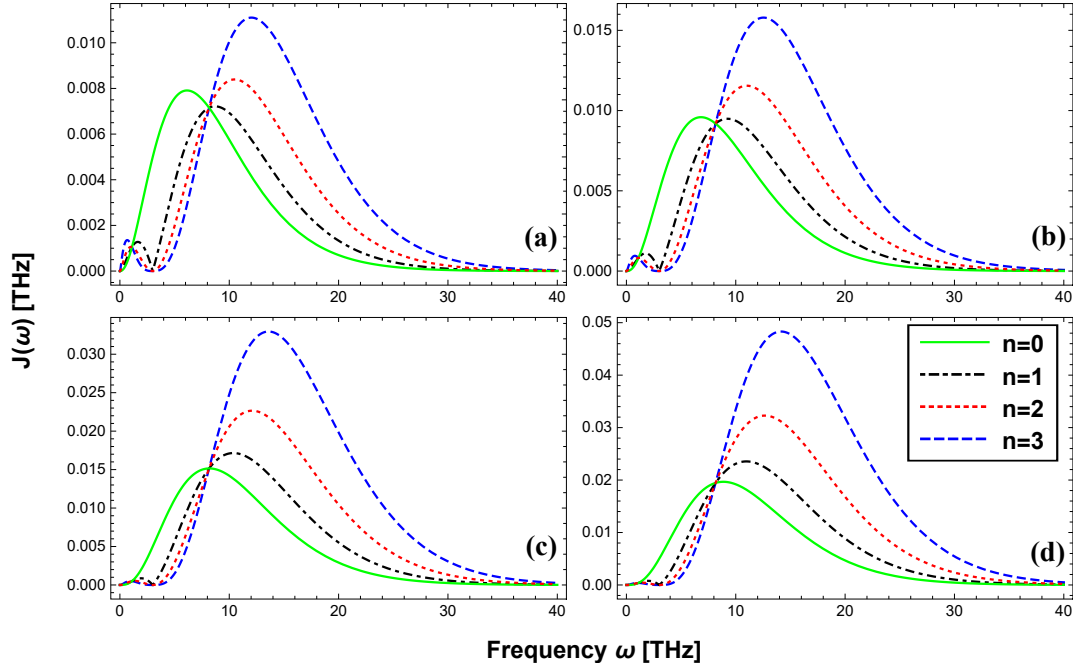


Figure 3.2: Spectral density functions of $J(\omega)$ for the values of (a) $\alpha=2.25$, (b) $\alpha=2.5$, (c) $\alpha=3$, (d) $\alpha=3.25$. Values of n are shown on the graphs. For each case we take $\omega_c = 3$ THz, $l=1.1$ and $q=0.005$.

erns how SDF scales linearly for low frequency bath modes. In fact, this form of SDFs can be used to construe a variety of relaxations which are slower than the exponential decay and faster or slower than the inverse power laws in quantum systems [51]. In Figure 3.2, we plot the SDFs of super-Ohmic environments for our analysis in this chapter.

3.3 Results and Discussion

Now, let's analyse the effect of these logarithmic perturbations in super-Ohmic environments to coherent resonance energy transfer and measure the performance of the formalized QME in Eq. (3.26). In order to do that, we plot the population at the donor site ($|X_1\rangle$) with respect to time (in ps). Donor population is extracted from the reduced density matrix using $P(t) = \langle X_1 | \hat{\sigma}(t) | X_1 \rangle$. It is

important to note that, the reduced density matrix utilized here is in the polaron frame and there is no requisite of that to be in the original frame, since donor population is unconstrained from bath's creation and annihilation operators, $e^G \hat{\sigma}_z e^{-G} = \hat{\sigma}_z$ [43–45, 58].

3.3.1 Performance on system-bath coupling strengths

To begin our analysis, let's consider a donor-acceptor pair which is associated with super-Ohmic environments with various system bath coupling strengths. Let's take $\alpha = 3$ for these super-Ohmic environments and SDF can be written as,

$$J_1(\omega) = q\omega_c \left(\frac{\omega}{\omega_c}\right)^3 \exp\left(\frac{-1.1\omega}{\omega_c}\right) \left|\ln\left(\frac{\omega}{\omega_c}\right)\right|^n, \quad (3.42)$$

where we change the value of q from (a) 0.005 to (b) 0.01 to (c) 0.03 to (d) 0.05. Results obtained for this case is given in Figure 3.3. In plot (a) where $q = 0.005$, we observe coherent dynamics for each value of the logarithmic perturbations where the system-bath coupling is very weak. It is evident that, as logarithmic perturbations are increasing the damping effect is also increasing. Full polaron based QME has performed well here as there are no distortions in the graphs.

In plot (b) when the system bath coupling is elevated to 0.01, we can observe a reduction in the magnitude of the oscillations and damping effect on $n = 0, 1$ and 2 is noticeable. Interesting fact to note here that, $n = 3$ graph is distorted and the infrared divergence effect has occurred. Hence, full polaron QME has failed to simulate the coherent transfer when the system-bath coupling is 0.01 and the logarithmic perturbation factor is 3.

When the system-bath coupling strength is further raised to 0.03 in plot (c), we can perceive that this distortion now occurs from $n = 2$ onwards. In addition, even if $n = 0$ and $n = 1$ graphs show coherent transfer dynamics, we observe a very strong damping effect for them. We discern in plot (d) that, all the graphs

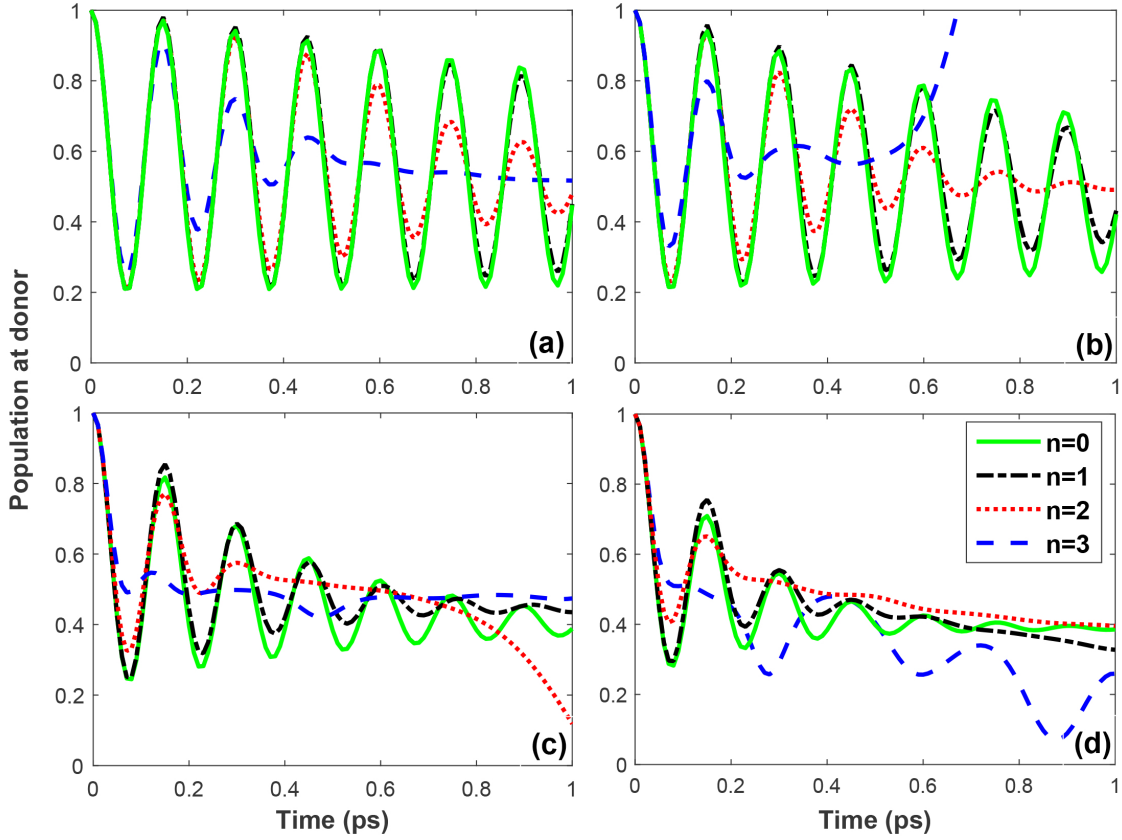


Figure 3.3: Population at donor for $J_1(\omega)$ super-Ohmic environment SDF with (a) $q=0.005$ (b) $q=0.01$ (c) $q=0.03$ and (d) $q=0.05$. For all cases, we consider $\alpha = 3$, $l = 1.1$, $\omega_c = 3$ THz, $\epsilon = 3$ THz, $V = 3$ THz, $\hbar = 1$ and $T = 300$.

except for $n = 0$, express infrared divergence effect where full polaron based QME is unable to manifest the coherent dynamics when the system-bath coupling strength is comparatively substantial. By observing the $n = 0$ graph for all the plots, we can corroborate that full polaron transformation-based is capable of predicting the coherent energy transfer dynamics for the considered range of system-bath coupling strength when there are no logarithmic perturbations. When observing plots (a) and (b) closely, it is evident that for weak system-bath coupling strengths, full polaron transformation-based QME is competent in showing coherent dynamics. But when system-bath coupling is stronger (in plots (c) and (d)), graphs show significant distortions when logarithmic perturbations are present.

Therefore, we can conclude that for environments with higher logarithmic perturbations cannot be utilized in conjunction with full polaron transformation-based QME to accurately describe the coherent energy transfer.

3.3.2 Performance on the Ohmicity parameter

Next we analyse how energy transfer transpires in different super-Ohmic environments (different values of the Ohmicity parameter) get affected due to logarithmic perturbations. The related SDF can be written as,

$$J_2(\omega) = 0.005\omega_c \left(\frac{\omega}{\omega_c}\right)^\alpha \exp\left(\frac{-1.1\omega}{\omega_c}\right) \left|\ln\left(\frac{\omega}{\omega_c}\right)\right|^n. \quad (3.43)$$

In Figure 3.4, we examine Ohmicity values from $\alpha = 2.25$ to $\alpha = 3.25$ where experienced logarithmic perturbations alter from (a) $n = 0$, (b) $n = 1$, (c) $n = 2$ to (d) $n = 3$. For all the graphs in plot (a), we observe higher oscillatory dynamics in environments with higher Ohmic value. Now we introduce logarithmic perturbations in the first order in plot (b). When comparing plot (a) and plot (b), it is evident that graphs of lower Ohmicity values ($\alpha = 2.25$ and $\alpha = 2.5$) have undergone considerable changes whereas graphs of higher Ohmicity values ($\alpha = 3$ and $\alpha = 3.25$) remain relatively unchanged. Therefore, we can identify that higher Ohmicity values show more resistance to logarithmic perturbations than the lower values. Furthermore, $\alpha = 2.25$ graph shows severe distortion due to infrared divergence effect.

When we raise the logarithmic perturbations to $n=2$ in plot (c), both $\alpha = 2.25$ and $\alpha = 2.5$ graphs have encountered severe distortions. Even-though, $\alpha = 3$ and $\alpha = 3.25$ graphs still show the coherent dynamics, the damping effect is very noticeable where latter shows less damping. In plot (d), besides the raised n value, overall behaviour remains the same. Nonetheless, the damping effect is significant for both $\alpha = 3$ and $\alpha = 3.25$ graphs.

Therefore, by observing all four plots we can deduce that, in a super-Ohmic environment with logarithmic perturbations, full polaron transformation-based QME is vulnerable and undergoes severe distortions when the Ohmicity parameter is a smaller value, whereas larger Ohmicity values manifest more immunity. Moreover, we discern significant damping effect for larger logarithmic factors.

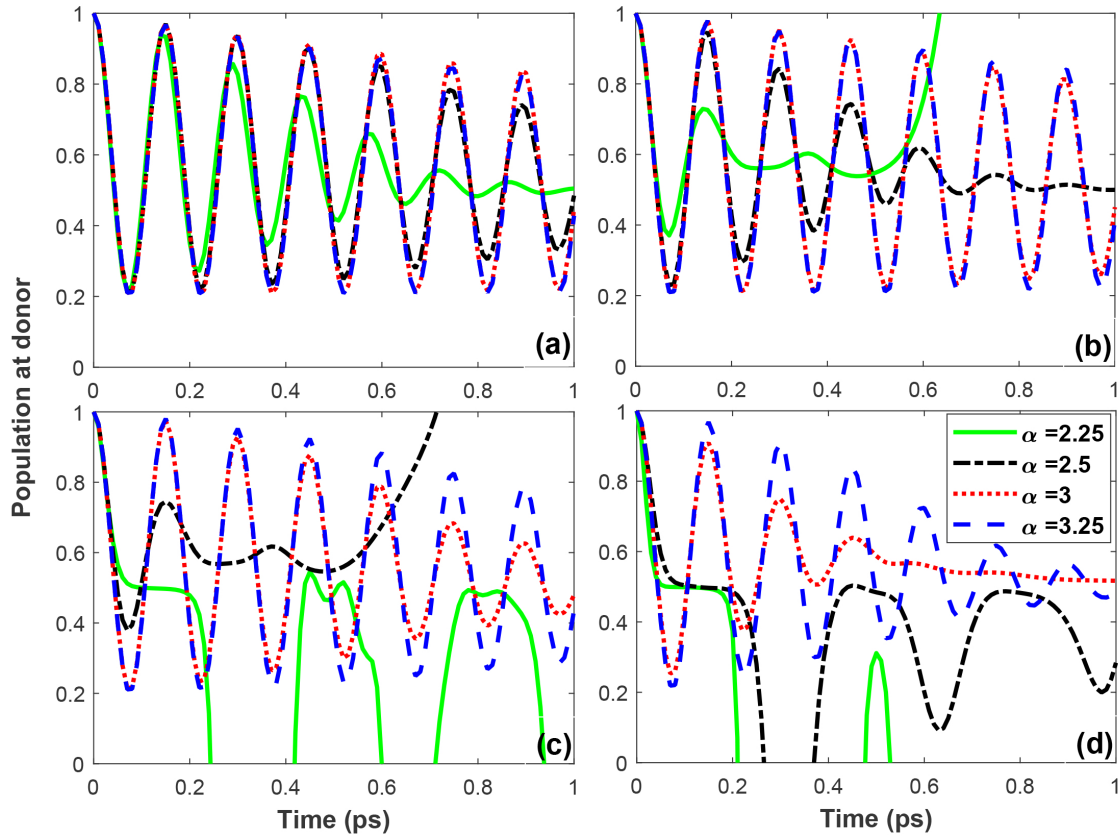


Figure 3.4: Population at donor for $J_2(\omega)$ super-Ohmic environment SDF where $\alpha = 2.25, \alpha = 2.5, \alpha = 3$ and $\alpha = 3.25$ for (a) $n = 0$, (b) $n = 1$, (c) $n = 2$ and (d) $n = 3$. For all cases, we consider $q=0.005, l = 1.1, \omega_c = 3$ THz, $\epsilon = 3$ THz, $V = 3$ THz, $\hbar = 1$ and $T = 300$.

3.4 Summary and Conclusions

In summary, we have investigated the role of logarithmic perturbations in super-Ohmic environments using a full polaron transformation-based time-local second-order quantum master equation. First, we have analysed the coherent resonance energy transfer dynamics through aforementioned QME in a variety of super-Ohmic environments by altering the system-bath coupling strengths. We have found that, in the weak system-bath coupling regime, results generated through the QME is acceptable. Nevertheless, when the system-bath coupling is large, for higher order logarithmic perturbations, QME is unable to predict the coherent oscillatory dynamics where it suffers significant distortions.

Subsequently, we have studied the performance of the full polaron transformation-based QME in different super-Ohmic environments experiencing logarithmic perturbations by varying the Ohmicity parameter. It has been observed that smaller Ohmicity values can suffer severe distortions even for a small logarithmic perturbation. On the other hand, larger Ohmicity values exhibit immunity even for a large logarithmic perturbation. Furthermore, as we increase the logarithmic perturbation factor, we observe a reduction in the magnitude of the oscillations for all the Ohmicity values considered in this study.

In conclusion, we have shown that full polaron transformation-based QME suffers infrared divergence when the Ohmicity value is smaller and when system-bath coupling strength is weaker in super-Ohmic environments with logarithmic perturbations. This study shows that, even though full polaron QME is shown to be capable of predicting coherent energy transfer dynamics in super-Ohmic environments, it is not consistently valid for an environment which experience logarithmic perturbations.

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Chapter 4

Significance of logarithmic perturbations in spectral density functions using variational polaron approach

4.1 Introduction

In the previous chapter, we studied a two-level donor-acceptor quantum system utilizing the full-polaron based quantum master equation. While we found that full-polaron based quantum master equation suffers from infrared divergence effect due to logarithmic perturbations, it could only be used in super-ohmic environments in the absence of these perturbations, due to the divergence of bath correlation functions owing to the full polaron approximation. In order to study the energy transfer dynamics accurately in perturbed ohmic and super-ohmic environments, we utilize the variational-polaron transformation based quantum master equation in this chapter for the quantum system shown in Figure 4.1. Contemporary research suggests that variational polaron transformation is far superior to full polaron transformation [58] and this chapter analyzes if the above fact holds true in disturbed quantum environments. In doing so, we attempt to understand the energy transfer dynamics manifest in such environments particularly their quantum coherence effects.

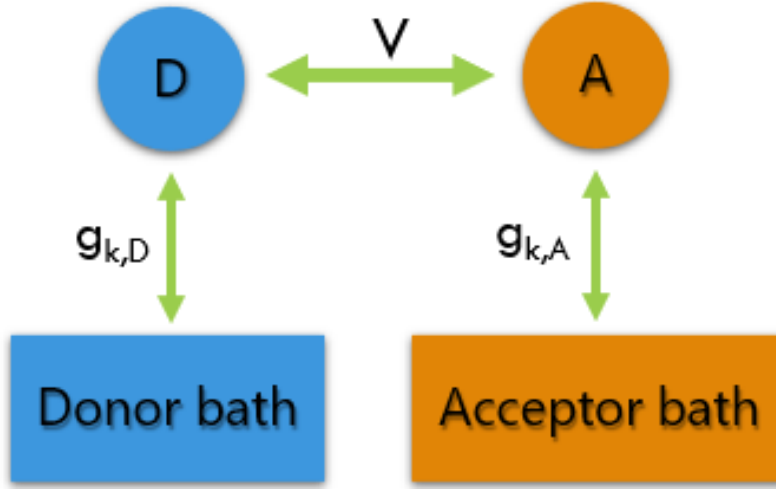


Figure 4.1: Donor chromophore(D) and an acceptor chromophore(A) are connected to identical and independent baths. V represents the inter-chromophore coupling whereas $g_{k,D}$ ($g_{k,A}$) represents the coupling between k^{th} bath mode and D (A) site.

This chapter is organized as follows. Following the introduction, in section 4.2, the formalism including the model and the analytical approach deployed for our analysis is outlined. In section 4.3, the results obtained for Ohmic like SDFs with logarithmic perturbations are discussed. Finally, section 4.4 summarizes and concludes this chapter.

4.2 Formalism

A two-level system consisting a donor (D) chromophore, an acceptor (A) chromophore and a bath of harmonic oscillators is considered. System and the environment are of the form of a spin boson model [43–45, 60]. Initially the entire system including the bath and other degrees of freedom are in thermal equilibrium in the ground state denoted by $|g\rangle$. Let's define $|D\rangle$ as the state where donor is excited and acceptor is in the ground state. $|A\rangle$ represents the same expression with respect to the acceptor. $|D\rangle$, $|A\rangle$ and $|g\rangle$ are the three states which com-

pletely describe the system.

A laser pulse [94] excites donor chromophore to $|D\rangle$ at $t=0$. Laser pulse has a duration of τ_{laser} and we assume $\tau_{laser} \ll \tau_{sd}$ where τ_{sd} is the spontaneous decay time to the ground. Under these circumstances, assuming separable states, the initial condition of the complete system can be written as,

$$\hat{\rho}(0) = \hat{\rho}_S(0) \otimes \frac{e^{-\beta \hat{H}'_b}}{Z}. \quad (4.1)$$

We assume the system to be a canonical ensemble and for a such an ensemble, the partition function can be written as $Z = \text{Tr}_b \{e^{-\beta \hat{H}'_b}\}$ by taking the trace over the bath degrees of freedom. Also, $\beta = 1/k_B T$ where k_B is the Boltzmann's constant and T is the temperature of the system in Kelvins. Also, $\hat{H}'_b$ defines the bath Hamiltonian. Since initially the system population is at $|D\rangle$, we write $\hat{\rho}_S(0) = |D\rangle \langle D|$.

4.2.1 System Hamiltonian

In order to write the system Hamiltonian, we first define Pauli operators $\hat{\sigma}_x = |D\rangle \langle A| + |A\rangle \langle D|$, $\hat{\sigma}_y = i(|D\rangle \langle A| - |A\rangle \langle D|)$ and $\hat{\sigma}_z = |D\rangle \langle D| - |A\rangle \langle A|$ [37,95]. After the application of the laser pulse, total Hamiltonian of the complete system can be written as,

$$\hat{H}' = \hat{H}'_p + \hat{H}'_c + \hat{H}'_b + \hat{H}'_{sb} \quad (4.2)$$

where $\hat{H}'_p = (\epsilon/2)\hat{\sigma}_z$ is the population Hamiltonian which represents the combine energy localized to each site of the quantum system. Here, the energy difference between $|D\rangle$ state and $|A\rangle$ state is given by $\epsilon = \epsilon_D - \epsilon_A$. Second term is the Hamiltonian of the coherences given by $\hat{H}'_c = V\hat{\sigma}_x$ where, V is the electronic coupling term between the two sites. This Hamiltonian captures the energy de-

localized between the two states. Third term is the bath Hamiltonian represented by $\hat{H}'_b = \sum_{j=D,A} \sum_k \hbar \omega_{k,j} \hat{b}_{k,j}^\dagger \hat{b}_{k,j}$ where the frequency of the k^{th} boson mode coupled to j^{th} site is denoted by $\omega_{k,j}$. The creation(annihilation) operator coupled to j^{th} site of k^{th} boson mode is written as $\hat{b}_{k,j}^\dagger$ ($\hat{b}_{k,j}$). Final term is the system-bath interaction Hamiltonian given by $\hat{H}'_{sb} = \sum_{j=D,A} |j\rangle \langle j| \sum_k \hbar \omega_{k,j} g_{k,j} (\hat{b}_{k,j}^\dagger + \hat{b}_{k,j})$. The system-bath coupling denoted by $g_{k,j}$ is for k^{th} bath attached to j^{th} site, which is fully described through the bath SDF $J(\omega)$ for a spin boson model [43–45, 60]. More details on SDF will be discussed later in Sec. 4.2.5. Now we can write the total Hamiltonian in the expanded form as,

$$\hat{H}' = \frac{\epsilon}{2} \hat{\sigma}_z + V \hat{\sigma}_x + \sum_{j=D,A} \sum_k \hbar \omega_{k,j} \hat{b}_{k,j}^\dagger \hat{b}_{k,j} + \sum_{j=D,A} |j\rangle \langle j| \sum_k \hbar \omega_{k,j} g_{k,j} (\hat{b}_{k,j}^\dagger + \hat{b}_{k,j}). \quad (4.3)$$

4.2.2 Polaron transformation

Consider the polaron generator function given by [43, 44, 58],

$$G = \sum_{j=D,A} |j\rangle \langle j| \sum_k \frac{f_{k,j}}{\hbar \omega_{k,j}} (\hat{b}_{k,j}^\dagger - \hat{b}_{k,j}) \quad (4.4)$$

where $f_{k,j}$ is the variational parameter in the range of $0 \leq f_k \leq g_k$. Now, we transform the free system Hamiltonian following $\hat{H} = e^G \hat{H}' e^{-G}$.

We now apply the variational polaron transformation to each Hamiltonian using the polaron generator function given in Eq. 4.4. First, let's apply the transformation into population Hamiltonian given by $\hat{H}_p = e^G \hat{H}'_p e^{-G}$. Since $\hat{H}'_p$ is independent of $\hat{b}_{k,j}$ and $\hat{b}_{k,j}^\dagger$, we obtain,

$$\hat{H}_p = \hat{H}'_p = \frac{\epsilon}{2} \hat{\sigma}_z \quad (4.5)$$

Then let's apply the transformation to coherence Hamiltonian given by $\hat{H}_c = e^G \hat{H}'_c e^{-G}$. Simplifying the equation using Baker–Campbell–Hausdorff formula,

we obtain,

$$\hat{H}_c = V |D\rangle \langle A| \exp\left(\frac{f_{k,D}}{\hbar\omega_{k,D}}(\hat{b}_{k,D}^\dagger - \hat{b}_{k,D})\right) + V |A\rangle \langle D| \exp\left(\frac{f_{k,A}}{\hbar\omega_{k,A}}(\hat{b}_{k,A}^\dagger - \hat{b}_{k,A})\right) \quad (4.6)$$

This can be rewritten using bath displacement operators as,

$$\hat{H}_c = VB(|D\rangle \langle A| + |A\rangle \langle D|) + V |D\rangle \langle A| \hat{B}_+ + V |A\rangle \langle D| \hat{B}_- - VB(|D\rangle \langle A| + |A\rangle \langle D|) \quad (4.7)$$

Simplifying further we reach,

$$\hat{H}_c = V_R \hat{\sigma}_x + \hat{H}_{\text{Displaced}} \quad (4.8)$$

Now we transform the bath Hamiltonian using $\hat{H}_b = e^G \hat{H}'_b e^{-G}$ where we reach,

$$\begin{aligned} \hat{H}_b = \hat{H}'_b + \sum_k \frac{f_{k,A}^2}{\hbar\omega_{k,A}} + \sum_k \frac{f_{k,D}^2}{\hbar\omega_{k,D}} - |D\rangle \langle D| \sum_k \hbar\omega_{k,j} f_{k,D} (\hat{b}_{k,D}^\dagger + \hat{b}_{k,D}) \\ - |A\rangle \langle A| \sum_k \hbar\omega_{k,j} f_{k,A} (\hat{b}_{k,A}^\dagger + \hat{b}_{k,A}) \end{aligned} \quad (4.9)$$

after simplifying using the Baker–Campbell–Hausdorff formula. Finally, we transform the system-bath Hamiltonian using $\hat{H}_{sb} = e^G \hat{H}'_{sb} e^{-G}$,

$$\begin{aligned} \hat{H}_{sb} = \sum_{j=D,A} |j\rangle \langle j| \sum_k \hbar\omega_{k,j} g_{k,j} (\hat{b}_{k,j}^\dagger + \hat{b}_{k,j}) - 2 |D\rangle \langle D| \sum_k \frac{f_{k,D} g_{k,D}}{\hbar\omega_{k,D}} \\ - 2 |A\rangle \langle A| \sum_k \frac{f_{k,A} g_{k,A}}{\hbar\omega_{k,A}} \end{aligned} \quad (4.10)$$

Total transformed Hamiltonian is given by,

$$\hat{H} = \hat{H}_p + \hat{H}_c + \hat{H}_b + \hat{H}_{sb} \quad (4.11)$$

which can be expressed as,

$$\hat{H} = \frac{1}{2}(\epsilon + R_D - R_A)\hat{\sigma}_z + V_R\hat{\sigma}_x + \hat{H}'_b + \frac{1}{2}(R_D + R_A)\mathbb{1} + \hat{H}_{\text{Linear}} + \hat{H}_{\text{Displaced}} \quad (4.12)$$

Subsequently, above equation can be written as $\hat{H} = \hat{H}_0 + \hat{H}_1$ where the zeroth order Hamiltonian is given by,

$$\hat{H}_0 = \frac{1}{2}(\epsilon + R_D - R_A)\hat{\sigma}_z + V_R\hat{\sigma}_x + \hat{H}'_b + \frac{1}{2}(R_D + R_A)\mathbb{1} \quad (4.13)$$

where,

$$R_j = \sum_k \frac{f_{k,j}}{\hbar\omega_{k,j}}(f_{k,j} - 2g_{k,j}) \quad (4.14)$$

is the polaron shifted site energy (a scalar) of the j^{th} site and $\mathbb{1}$ represents the 2x2 identity matrix. First order interaction Hamiltonian is given by $\hat{H}_1 = \hat{H}_{\text{Linear}} + \hat{H}_{\text{Displaced}}$. Linear portion of the interaction Hamiltonian is of the form,

$$\hat{H}_{\text{Linear}} = \sum_{j=D,A} |j\rangle \langle j| \sum_k \hbar\omega_{k,j} (g_{k,j} - f_{k,j}) (\hat{b}_{k,j}^\dagger + \hat{b}_{k,j}). \quad (4.15)$$

Notice by changing f_k in the range of $0 \leq f_k \leq g_k$, one can change the perturbation arising from $\hat{H}_{\text{Linear}}$. Displaced Hamiltonian $\hat{H}_{\text{Displaced}}$ derived in terms of bath displacement operators through $\hat{B}_x = (1/2)(\hat{B}_- + \hat{B}_+ - 2B)$ and $\hat{B}_y = (i/2)(\hat{B}_+ - \hat{B}_-)$ is of the form,

$$\hat{H}_{\text{Displaced}} = V (\hat{\sigma}_x \hat{B}_x + \hat{\sigma}_y \hat{B}_y) \quad (4.16)$$

The terms $\hat{B}_x$ and $\hat{B}_y$ are written in terms of $\hat{B}_\pm = \hat{B}_{\pm,D} \hat{B}_{\mp,A}$ where,

$$\hat{B}_{\pm,j} = \exp \left[\pm \sum_k \frac{f_{k,j}}{\hbar\omega_{k,j}} (\hat{b}_{k,j}^\dagger - \hat{b}_{k,j}) \right] \quad (4.17)$$

with $j=D,A$ and B is the expectation value of $\hat{B}_\pm$ given by,

$$B = \exp \left[-\frac{1}{2} \sum_j \sum_k \frac{f_{k,j}^2}{\hbar^2 \omega_{k,j}^2} \coth \left(\frac{\hbar \beta \omega_{k,j}}{2} \right) \right]. \quad (4.18)$$

Notice that, in the original frame, contribution of the system-bath interaction Hamiltonian is much greater to the total system Hamiltonian, compared to the variational polaron transformed interaction Hamiltonian due to the introduction of the variational parameter $f_{k,j}$. We have reduced the contribution of the interaction Hamiltonian in the polaron transformed frame in order to treat it as a perturbation. The main reason for variational theory performing better than the full polaron transformation is due to the term $\hat{H}_{\text{Linear}}$. In the full polaron transformation we take $g_{k,j} = f_{k,j}$ by definition and thereby making $\hat{H}_{\text{Linear}} = 0$. For a relatively large system-bath coupling, full polaron transformation cannot effectively represent the interaction term by just $\hat{H}_{\text{Displaced}}$ term because it lacks the contribution of $\hat{H}_{\text{Linear}}$. This is the reason why full polaron transformation suffers from infra-red divergence in Ohmic environments [61]. In addition, $\hat{H}_{\text{Displaced}}$ term captures the energy of bath displacement operators after the polaron transformation. Further, the electronic coupling term V appearing in the free Hamiltonian in Eq. (4.3) is now renormalized after performing the polaron transformation. It is now defined as $V_R = VB$.

We now assume that the baths attached to each site are identical, which yields $R_D = R_A = R = \sum_k f_k (\hbar \omega_k)^{-1} (f_k - 2g_k)$, $f_{k,j} = f_k$, $g_{k,j} = g_k$ and $\omega_{k,j} = \omega_k$. Zeroth Hamiltonian then becomes,

$$\hat{H}_0 = \frac{\epsilon}{2} \hat{\sigma}_z + V_R \hat{\sigma}_x + \hat{H}'_b + R \mathbb{1} \quad (4.19)$$

and the expectation value of $\hat{B}_\pm$ becomes,

$$B = \exp \left[- \sum_k \frac{f_k^2}{\hbar^2 \omega_k^2} \coth \left(\frac{\hbar \beta \omega_k}{2} \right) \right] \quad (4.20)$$

4.2.3 Free energy minimization

As mentioned earlier, term f_k appearing in above equations can be in the range of $0 \leq f_k \leq g_k$. We choose an exact value for f_k in order to minimize the contribution of $\hat{H}_1$ to free energy, so that second-order perturbation theory can be applied.

In order to find the variational parameters f_k appearing in the interaction Hamiltonian ($\hat{H}_1$) defined above, we use Feynman-Bogoliubov upper bound on the free energy [59] as been shown in [43, 44]. Feynman-Bogoliubov upper bound on the free energy is given by,

$$A_{\text{FB}} = -\frac{1}{\beta} \ln \left[\text{Tr} \left\{ e^{-\beta \hat{H}_0} \right\} \right] + \langle \hat{H}_1 \rangle_{\hat{H}_0} + O \left(\langle \hat{H}_1^2 \rangle_{\hat{H}_0} \right). \quad (4.21)$$

A much improved version of free energy minimization argument has been introduced and can be found in [60]. True free energy A is related to A_{FB} through the inequality $A_{\text{FB}} \geq A$ and the second term of Eq. (4.21) is zero by construction.

$$A_{\text{FB}} = R - \frac{1}{\beta} \ln \left[2 \cosh \left(\frac{\beta \eta}{2} \right) \right] \quad (4.22)$$

Here, $\eta = \sqrt{\epsilon^2 + 4V_R^2}$. By taking the derivative of A_{FB} with respect to f_k in order to minimize the free energy,

$$\frac{\partial A_{\text{FB}}}{\partial f_k} = \frac{\partial A_{\text{FB}}}{\partial R} \frac{\partial R}{\partial f_k} + \frac{\partial A_{\text{FB}}}{\partial B} \frac{\partial B}{\partial f_k} = 0 \quad (4.23)$$

we arrive at,

$$F(\omega_k) = \left[1 + \frac{2V_R^2}{\eta\hbar\omega_k} \tanh\left(\frac{\beta\eta}{2}\right) \coth\left(\frac{\hbar\beta\omega_k}{2}\right) \right] \quad (4.24)$$

and $f_k = g_k F(\omega_k)$. We introduce the form of SDF as $J(\omega) = \sum_k g_k^2 \delta(\omega - \omega_k)$. Then the expectation value of $\hat{B}_\pm$ becomes,

$$B = \exp \left[- \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} F^2(\omega) \coth\left(\frac{\hbar\beta\omega}{2}\right) \right] \quad (4.25)$$

assuming a continuous bath. Since renormalized coupling term $V_R = VB$ and B is a function of V_R itself, through $F(\omega_k)$, to find V_R these equations should be solved self consistently.

4.2.4 Quantum Master Equation (QME)

To develop the quantum master equation (QME), we consider quantum Liouville operators which define the state evolution of a quantum system over time [40]. System density matrix ($\hat{\rho}(t)$) and corresponding quantum Liouville operator ($\hat{\mathcal{L}}$) are related by,

$$\frac{d\hat{\rho}(t)}{dt} = -i\hat{\mathcal{L}}\hat{\rho}(t) = -i[\hat{\rho}(t), \hat{H}] \quad (4.26)$$

Up to this point all equations are in Schrödinger picture where only states of the system carried time dependence not the operators. But it is useful to change into the interaction (Dirac) picture of $\hat{H}_0$ in order to apply the perturbation theory. In the interaction picture of $\hat{H}_0$ we obtain,

$$\hat{\rho}_I(t) = e^{i\hat{\mathcal{L}}_0(t)t} \hat{\rho}(t) \quad (4.27)$$

where $\hat{\mathcal{L}}_0$ is the quantum Liouville operator related to zeroth order Hamiltonian $\hat{H}_0$ and $\hat{\rho}_I(t)$ is the density matrix in the interaction picture. By differentiating

with respect to time we then find,

$$\frac{d\hat{\rho}_I(t)}{dt} = -i [\hat{\rho}_I(t), \hat{H}_{1,I}(t)] = -i\hat{\mathcal{L}}_{1,I}(t)\hat{\rho}_I(t) \quad (4.28)$$

We define $\hat{\mathcal{L}}_{1,I}$ as the Liouville operator for $\hat{H}_{1,I}(t)$ where,

$$\hat{H}_{1,I}(t) = e^{i\hat{H}_0 t} \hat{H}_1 e^{-i\hat{H}_0 t} \quad (4.29)$$

which is the first order interaction Hamiltonian in the interaction picture. We now extract the system (or the relevant) component using standard projection operator method [55] defined by $\mathcal{P}(\cdot) \equiv \hat{\rho}_b \text{Tr}_b\{\cdot\}$ and the complimentary projection $\mathcal{Q}(\cdot) = (I - \mathcal{P})(\cdot)$ extracts the irrelevant part of the density matrix which is the bath. We apply projection operator mechanism to Eq. (4.28) and by simplifying we arrive at,

$$\frac{d\hat{\rho}_I(t)}{dt} = -i\mathcal{P}\hat{\mathcal{L}}_{1,I}(t) \left(\hat{\rho}_I(0) - i \int_0^t \hat{\mathcal{L}}_{1,I}(\tau) \hat{\rho}_I(\tau) d\tau \right) \quad (4.30)$$

Here, $\mathcal{P}\hat{\mathcal{L}}_{1,I}(t)\mathcal{P}\hat{\rho}_I(0) = 0$ since $\hat{H}_0$ and $\hat{H}_b$ commutes with each other. Also, $\mathcal{Q}\hat{\rho}_I(0) = \mathcal{Q}\hat{\rho}(0)$ according to Eq. (4.27). Then Eq. (4.30) becomes,

$$\mathcal{P} \frac{d\hat{\rho}_I(t)}{dt} = -i\mathcal{P}\hat{\mathcal{L}}_{1,I}(t)\mathcal{Q}\hat{\rho}_I(0) - \int_0^t \mathcal{P}\hat{\mathcal{L}}_{1,I}(t)\hat{\mathcal{L}}_{1,I}(\tau) (\mathcal{P}\hat{\rho}_I(\tau) + \mathcal{Q}\hat{\rho}(0)) d\tau \quad (4.31)$$

Regarding $\hat{\mathcal{L}}_{1,I}(t)$ we have made second-order approximation without substituting further for $\hat{\rho}_I(\tau)$ in Eq. (4.30). We define the reduced density matrix as $\hat{\sigma}_I(t) = \text{Tr}_b\{\hat{\rho}_I(t)\} = \mathcal{P}\hat{\rho}_I(t)$ which leads to,

$$\frac{d\hat{\sigma}_I(t)}{dt} = \hat{\mathcal{I}}(t) - \hat{\mathcal{R}}(t)\hat{\sigma}_I(t) \quad (4.32)$$

where,

$$\hat{\mathcal{R}}(t) = \int_0^t \text{Tr}_b \hat{\mathcal{L}}_{1,I}(t) \hat{\mathcal{L}}_{1,I}(\tau) \hat{\rho}_b d\tau \quad (4.33)$$

is the homogeneous term which relates to the system component and

$$\hat{\mathcal{I}}(t) = -i \text{Tr}_b \hat{\mathcal{L}}_{1,I}(t) \mathcal{Q} \hat{\rho}(0) - \int_0^t \text{Tr}_b \hat{\mathcal{L}}_{1,I}(t) \mathcal{Q} \hat{\mathcal{L}}_{1,I}(\tau) \hat{\rho}(0) d\tau \quad (4.34)$$

is the initial state dependent inhomogeneous term. As the interaction Hamiltonian $\hat{H}_1$ consists of two terms, second-order QME has two time correlation functions. We decompose $\hat{H}_1 = \sum_1^4 \hat{A}_i \otimes \hat{B}_i$ with $\hat{A}_1 = |D\rangle \langle D|$, $\hat{A}_2 = |A\rangle \langle A|$, $\hat{A}_3 = \hat{\sigma}_x$ and $\hat{A}_4 = \hat{\sigma}_y$ which are system operators where as $\hat{B}_i = \sum_k (g_k - f_k) (\hat{b}_{k,i}^\dagger + \hat{b}_{k,i})$ for $i=1,2$, $\hat{B}_3 = V\hat{B}_x$ and $\hat{B}_4 = V\hat{B}_y$ are bath operators.

We simplify the Eq. (4.32) using the definition of quantum Liouville operators to obtain the following form for the homogeneous part of the QME in the Schrödinger picture,

$$\begin{aligned} \hat{\mathcal{R}}(t) \hat{\sigma}(t) = & i [\hat{H}_S, \hat{\sigma}(t)] + \frac{1}{2} \sum_{i,j} \sum_{\omega} \mathcal{Y}_{ij}(\omega, t) \left[\hat{A}_i, \hat{\Delta}_{j,\omega} \hat{\sigma}(t) - \hat{\sigma}(t) \hat{\Delta}_{j,\omega}^\dagger \right] \\ & + i \sum_{i,j} \sum_{\omega} \mathcal{S}_{ij}(\omega, t) \left[\hat{A}_i, \hat{\Delta}_{j,\omega} \hat{\sigma}(t) + \hat{\sigma}(t) \hat{\Delta}_{j,\omega}^\dagger \right] \end{aligned} \quad (4.35)$$

where $\mathcal{Y}_{ij} = 2\text{Re}[K_{ij}(\omega, t)]$ and $\mathcal{S}_{ij} = \text{Im}[K_{ij}(\omega, t)]$ with,

$$K_{ij}(\omega, t) = \int_0^t d\tau \Lambda_{ij}(\tau) e^{i\hbar\omega\tau} \quad (4.36)$$

where $\Lambda_{ij}(\tau)$ are the bath correlation functions which can be calculated using $\Lambda_{ij}(\tau) = \text{Tr}_B \{ \hat{B}_{i,I}(\tau) \hat{B}_{j,I}(0) \hat{\rho}_R \}$. Terms $\hat{B}_{i,I}$ and $\hat{B}_{j,I}$ are bath operators in the interaction picture. Simplified final versions of $\Lambda_{ij}(\tau)$ are given below. When $i=1,2$

we find,

$$\Lambda_{11}(\tau) = \Lambda_{22}(\tau) = \int_0^\infty d\omega J(\omega)(1 - F(\omega))^2 \left(\cos(\hbar\omega\tau) \coth\left(\frac{\hbar\beta\omega}{2}\right) - i \sin(\hbar\omega\tau) \right) \quad (4.37)$$

and $\Lambda_{12}(\tau) = \Lambda_{21} = 0$ which prompt us of the bath correlation functions of Redfield theory. For $i=3$ we obtain,

$$\Lambda_{33}(\tau) = \frac{V_R^2}{2} \left(e^{\Phi(\tau)} + e^{-\Phi(\tau)} - 2 \right) \quad (4.38)$$

and $\Lambda_{34}(\tau) = \Lambda_{43}(\tau) = 0$. For $i=4$ we get,

$$\Lambda_{44}(\tau) = \frac{V_R^2}{2} \left(e^{\Phi(\tau)} - e^{-\Phi(\tau)} \right) \quad (4.39)$$

where,

$$\Phi(\tau) = 2 \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} F^2(\omega) \left(\cos(\hbar\omega\tau) \coth\left(\frac{\hbar\beta\omega}{2}\right) - i \sin(\hbar\omega\tau) \right) \quad (4.40)$$

which are similar to the bath correlation function form of full polaron transformation [45]. Further, $\Lambda_{14}(\tau) = \Lambda_{42}(\tau) = i\Lambda_c(\tau)$ and $\Lambda_{24}(\tau) = \Lambda_{41}(\tau) = -i\Lambda_c(\tau)$ where,

$$\Lambda_c(\tau) = V_R \int_0^\infty d\omega \frac{J(\omega)}{\omega} (F(\omega)(1 - F(\omega))) \left(\sin(\hbar\omega\tau) \coth\left(\frac{\hbar\beta\omega}{2}\right) + i \cos(\hbar\omega\tau) \right) \quad (4.41)$$

are unique to variational polaron transformation and stems from the product of $\hat{H}_{Linear}$ and $\hat{H}_{Displaced}$. Further, terms $\Lambda_{13}(\tau) = \Lambda_{31}(\tau) = \Lambda_{32}(\tau) = \Lambda_{23}(\tau) = 0$.

Further, $\hat{H}_S$ present in Eq. (4.35) is the Hamiltonian of the reduced density matrix in the Schrödinger picture. We find the eigenvectors and eigenoperators of $\hat{H}_S$

as $\hat{H}_S |\pm\rangle = (1/2)(2R \pm \eta) |\pm\rangle$. To obtain $\hat{\Delta}_{j,\omega}$ terms present in Eq. (4.35) we decompose system operators $\hat{A}_i$ to obtain,

$$\hat{\Delta}_{i,\omega} = \sum_{E'-E=\omega} |E\rangle \langle E| \hat{A}_i |E'\rangle \langle E'| \quad (4.42)$$

which satisfy the identity $\hat{A}_i = \sum_{\omega} \hat{\Delta}_{i,\omega}$. The terms $\hat{\Delta}_{i,\omega}$ takes the summation of all eigenvalues of $\hat{H}_S$ with a fixed energy difference of ω . Here $\omega = 0, \pm\eta$. Eigenoperators of the decomposed system operators are given by,

$$\hat{\Delta}_{1,\eta} = -\cos\theta \sin\theta |-\rangle \langle +| \quad (4.43)$$

$$\hat{\Delta}_{1,0} = \sin^2\theta |-\rangle \langle -| + \cos^2\theta |+\rangle \langle +| \quad (4.44)$$

$$\hat{\Delta}_{2,\eta} = \cos\theta \sin\theta |-\rangle \langle +| \quad (4.45)$$

$$\hat{\Delta}_{2,0} = \cos^2\theta |-\rangle \langle -| + \sin^2\theta |+\rangle \langle +| \quad (4.46)$$

$$\hat{\Delta}_{3,\eta} = \cos 2\theta |-\rangle \langle +| \quad (4.47)$$

$$\hat{\Delta}_{3,0} = \sin 2\theta (|+\rangle \langle +| - |-\rangle \langle -|) \quad (4.48)$$

$$\hat{\Delta}_{4,\eta} = i |-\rangle \langle +| \quad (4.49)$$

$$\hat{\Delta}_{4,0} = 0 \quad (4.50)$$

where $\theta = (1/2) \arctan(2V_R/\epsilon)$. Also, for all cases $\hat{\Delta}_{i,-\eta} = \hat{\Delta}_{i,\eta}^\dagger$ identity is true.

The inhomogeneous term in Eq. (4.32) depends on the initial state of the irrelevant component $\mathcal{Q}\hat{\rho}(0)$ which is given by,

$$\begin{aligned} \mathcal{Q}\hat{\rho}(0) &= (1 - \mathcal{P}) \left(e^G |1\rangle \langle 1| \otimes \hat{\rho}_B(0) e^{-G} \right) \\ &= |1\rangle \langle 1| \otimes (\hat{\rho}_b - \hat{\rho}_R) \end{aligned} \quad (4.51)$$

where $\hat{\rho}_B(0)$ is the initial bath density matrix and $\hat{\rho}_b$ provides the variationally transformed initial bath density matrix. If we were to select a reference bath density matrix $\hat{\rho}_R = \hat{\rho}_b$, it vanishes the inhomogeneous term which has been the assumption for our analysis.

4.2.5 Spectral density function

As elucidated earlier, the SDF governs how strong each site is attached to each mode in the bath of harmonic oscillators. Therefore, in general, SDF decides if an energy transfer is coherent or incoherent in nature through the bath relaxation times. Most previous studies [43, 44, 58] of variationally polaron transformed master equation were of the standard form of spectral densities given by $J(\omega) = q\omega_c^{1-\alpha}\omega^\alpha e^{-\omega/\omega_c}$, where q is the bath coupling strength and ω_c is the cut-off frequency. The parameter α decides the frequency response of the spectral density and values $\alpha < 1$, $\alpha > 1$, $\alpha = 1$ corresponds to sub-Ohmic, super-Ohmic and Ohmic environments [61], respectively.

Few alternative SDFs have also been studied such as in [96] and [97]. It has been shown that log-normal type spectral density presented in [52] can replicate the shape of the spectral densities obtained through experimental efforts more precisely than other types. This form has two adjustable parameters (cut-off frequency ω_c and standard deviation σ_{SD}) that can be used in order to fit to a given shape. The form of log-normal SDF can be written as,

$$J(\omega) = q \exp \left\{ -\frac{1}{2\sigma_{SD}^2} \left[\ln \left(\frac{\omega}{\omega_c} \right) \right]^2 \right\}. \quad (4.52)$$

The exponential term present in the above equation can be written as a sum of logarithmic terms of various orders. Fundamentally, logarithmic decay present in the log-normal format is physically different from exponential cut-off present

in Ohmic like SDFs. In light of these developments, logarithmic decays can be used to perturb Ohmic like SDFs in order to represent systems which are slightly deviated from the original form. Our purpose of this chapter is to analyse such a SDF given in [51] (see figure description of Figure. 1) of the form,

$$J(\omega) = q\omega_c \left(\frac{\omega}{\omega_c}\right)^\alpha \exp\left(\frac{-l\omega}{\omega_c}\right) \left|\ln\left(\frac{\omega}{\omega_c}\right)\right|^n \quad (4.53)$$

where terms α , l and n govern how strong each decay form affects the spectral density. The Ohmicity parameter is given by α and it decides the type of the environment defined by the SDF. Further, long-time decoherence or re-coherence process and the information backflow are uniquely governed by this parameter [51]. Parameter l governs how rapid and steep the exponential decay is and n is the factor of the power law profile for logarithmic perturbations.

An experiment conducted in [98], shows that a trapped impurity in a double-well potential, surrounded by a cold gas, can replicate a qubit interacting with an Ohmic-like environment under certain conditions whereby the corresponding SDF changes from sub-Ohmic to Ohmic to super-Ohmic when scattering length of the bosons in the environment is been changed. These type of changing environments do not necessarily follow the exact shape of the SDF produced by conventional sub-Ohmic, Ohmic and super-Ohmic functions. In such scenarios, SDF given in Eq. 4.53 can capture the irregularities and defections in the frequency domain when the environment of a quantum system is constantly changing. Also, this feasible form of logarithmic and Ohmic-like SDF subsumes low frequency power-law profiles obtained by removable logarithmic singularities. Therefore, this form of SDFs can be used to interpret a large range of relaxations which are slower than the exponential decay and faster or slower than the inverse power laws in quantum systems [51]. In Figure.4.2, the SDFs in the form of Eq. (4.53) is plotted for different values of the Ohmicity parameter that we used to generate

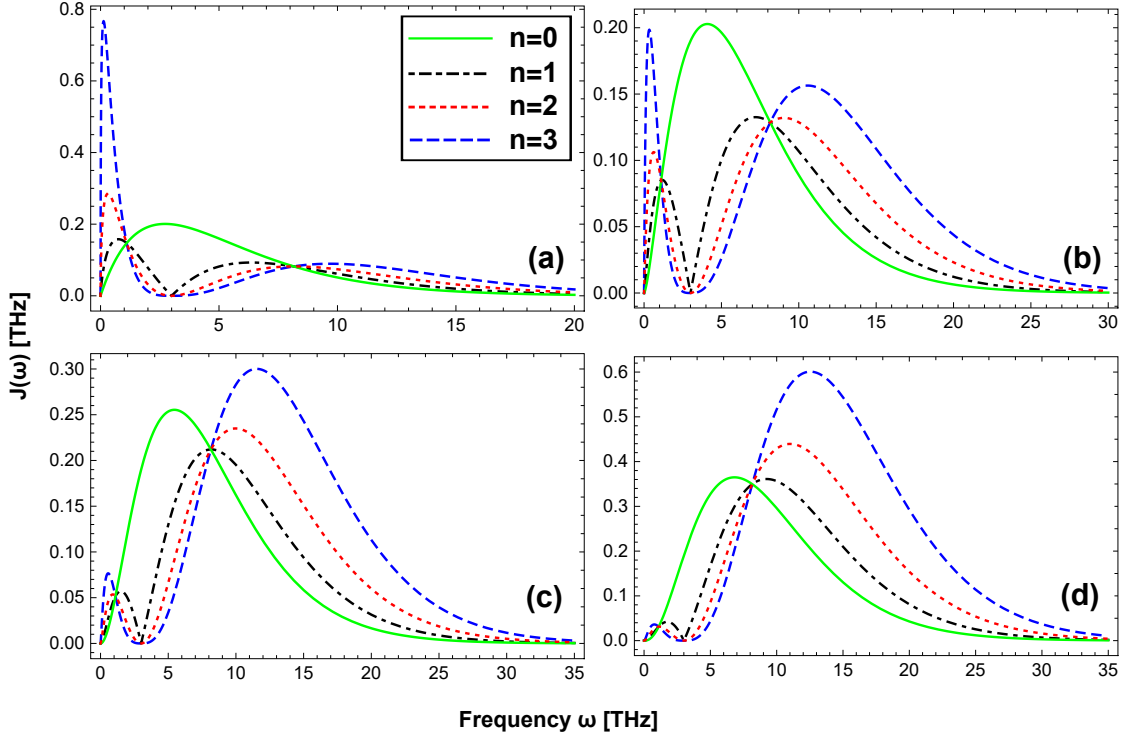


Figure 4.2: Spectral density functions of $J(\omega)$ for the values of (a) $\alpha=1$, (b) $\alpha=1.5$, (c) $\alpha=2$, (d) $\alpha=2.5$. Values of n are shown on the graphs. For each case we take $\omega_c = 3$ THz, $l=1.1$ and $q=0.2$.

results.

We plot several of the logarithmic SDF functions for various α and n values in Figure 4.2. We observe that for each value of α , all of the $J_{\alpha,n}$ functions intersect at $\omega = \omega_c/e$ and at $\omega = \omega_c e$. This naturally suggests the division of the frequency space into three regions:

- The low-frequency range $(0, \omega_c/e)$, in which $J_{\alpha,n_1} < J_{\alpha,n_2}$ for all $n_1 < n_2$.
- The intermediate range $(\omega_c/e, \omega_c e)$, in which $J_{\alpha,n_1} < J_{\alpha,n_2}$ for all $n_1 > n_2$.
- The high-frequency range $(\omega_c e, \infty)$, in which $J_{\alpha,n_1} < J_{\alpha,n_2}$ for all $n_1 < n_2$.

We also note here that the total damping of the oscillatory system due to the bath can be quantified as the total energy exchange between the system and the bath, which is equal to the total coupling of the system with the continuum of bath

states. This in turn can be quantified by the area under the $J_{\alpha,n}$ curves. For Ohmic environments, the area under the curves for $J_{0,0}$ is more than $J_{0,1}$ and $J_{0,2}$, but is less than $J_{0,3}$ and $J_{0,4}$. This suggests a unique relationship between the relative damping effected by these SDFs on the system. For much larger α values, the area under the curve for $J_{\alpha,0}$ is much less than that for $J_{\alpha,n}$ for $n > 0$. As we shall see later, these factors become significant in determining whether the donor-acceptor system experiences coherent interactions or incoherent decays. As an example, for systems described by SDFs with larger comparable areas, the energy transfer dynamics between the donor and acceptor takes the form of a highly damped oscillator. In addition to this, it is important to note that due to the presence of logarithmic factors, the coupling around the cut-off frequency of the environment is less significant. When there are no logarithmic perturbations, we see a larger coupling around the area of the cut-off frequency of the environment.

4.3 Results and Discussion

Let's investigate how different versions of Ohmic like spectral densities with logarithmic perturbations can affect the energy transfer dynamics of quantum systems. To this purpose, we use Eq. (4.35) with different SDFs as elucidated in the following sections. Note that Eq. (4.35) is in the polaron frame. Since the population Hamiltonian is independent of bath creation and annihilation operators, $e^G \hat{\sigma}_z e^{-G} = \hat{\sigma}_z$, the donor population extracted using the reduced density matrix,

$$P_D(t) = \langle D | \hat{\sigma}(t) | D \rangle \quad (4.54)$$

has no requirement of converting into the original frame [43–45,58]. For our analysis below, values for q and l are chosen in order to show the range of variations in energy transfer dynamics due to these logarithmic perturbations. We take $l=1.1$,

$\omega_c = 3$ THz, $\epsilon = 3$ THz, $V = 3$ THz and $T = 300$ K for the analysis.

4.3.1 Super-Ohmic environments

To begin our analysis, we first consider a donor and acceptor system where each site is coupled to identical and independent super-Ohmic baths as previously studied using the polaron frame in [43–45,55,58]. Consider the SDF of the form,

$$J_2(\omega) = q\omega_c \left(\frac{\omega}{\omega_c}\right)^{1.5} \exp\left(\frac{-1.1\omega}{\omega_c}\right) \left|\ln\left(\frac{\omega}{\omega_c}\right)\right|^n. \quad (4.55)$$

We obtain Figure 4.3 by changing the factor of bath coupling strength q for $n=0$, $n=1$, $n=2$ and $n=3$ cases of the above SDF. Our objective is to investigate how the effects of logarithmic perturbations introduced by n vary for different factors of bath coupling strengths.

In plot (a), the bath coupling factor q has a relatively large value of $q=0.3$. When $n=0$, we see that coherent dynamics are present and the amount of coherence is less than that of when $n=1$ and $n=2$. This is due to latter two cases having a weaker overall coupling compared to $n=0$ case (black and red plots have lower area compared to the green plot of Figure 4.2(b)). In the cases of $n=0,1$ and 2 , observed coherence behaviour is much alike due to the similarities in the areas under the respective curves according to the Figure 4.2 (comparing green, black and red plots of Figure 4.2(b)). The fact that both $n=1$ and $n=2$ graphs show similar peaks in the dynamics is an interesting observation. But the logarithmic perturbations have reduced the oscillatory behaviour in the latter due to the larger area under the curve for $n=2$ graph (refer to the red plot of Figure 4.2(b)). In the case of $n=3$, quantum coherence (or tunnelling) effects are no longer visible where higher order of logarithmic perturbations have completely damped the oscillatory dynamics due to the largest area out of all SDFs (The blue plot has the largest area compared to green, black and red plots of Figure 4.2(b)). For all cases

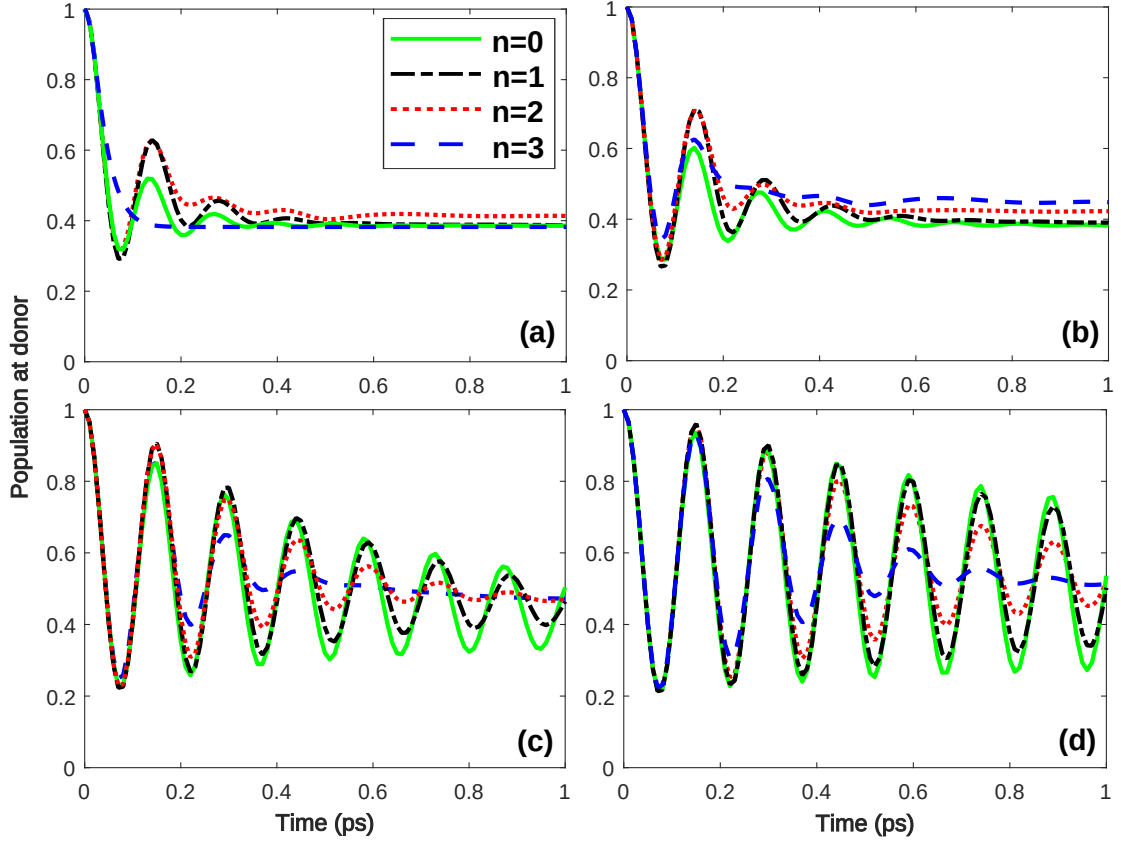


Figure 4.3: Population at donor for $J_2(\omega)$ super-Ohmic environment SDF with (a) $q=0.3$ (b) $q=0.2$ (c) $q=0.05$ and (d) $q=0.02$. For all cases $\alpha = 1.5$, $l = 1.1$, $\omega_c = 3$ THz, $\epsilon = 3$ THz, $V = 3$ THz and $T = 300$ K has been considered.

in plot (a), steady state donor population remains the same. Plot (b) of Figure 4.3 is for $q=0.2$. Interestingly, we see an increase of coherence behaviour across all plots due to the smaller bath coupling strength compared to the previous case. In the graph for $n=0$, compared to $n=1$ and $n=2$ graphs, oscillatory effect is less due to the weaker overall damping of the latter two environments. The most oscillatory behaviour is shown by the graph for $n=1$ out of all four graphs. This is due to having a weaker overall coupling compared to other cases. Unlike before, $n=2$ graph neither share the same peaks nor the quantum coherence effects with graph for $n=1$ due to the variations occurred to both high frequency response and low frequency response by reducing the system bath coupling (q). In addition, for

the case of $n=3$, a small oscillation can be observed. As for the steady state donor population value, all four graphs are comparable.

We decrease the bath coupling strength even further to $q=0.05$ for plot (c). Owing to the smaller q value, all four graphs shows quantum coherence effects. Interestingly for the cases of $n=0$ and $n=1$, we see that the donor population undergoes considerably large oscillations, while sharing relatively the same maxima and minima due to the similarities in the SDFs. For $n=2$, coherence effects are relatively damped compared to $n=0$ or $n=1$ due to larger overall coupling of $n=2$ compared to the latter two. In the case of $n=3$, oscillatory dynamics vanishes after 0.7 ps where it exhibits the most damping effect out of the four graphs.

Plot (d) corresponds to the case of $q=0.02$ where the bath coupling factor is relatively very small. For $n=0$ and $n=1$, considerable oscillations are present. In fact the minima and maxima for those two cases agrees with each other for the considered time period due to the similarities in the SDFs. The case of $n=2$ exhibits an increase of damped oscillations over time and for $n=3$, the level of damping effect is very noticeable.

Therefore, in the case of super-Ohmic environment, as the factor of logarithmic perturbation increases from 0 to 3, quantum coherence effects reduces considerably over time for smaller q values as shown in plot (c) and plot (d) in Figure 4.3. An interesting case to note that, this pattern is consistent for the case of larger q values for $n=1,2$ and 3 as exhibited in plot (a) and plot (b). The case of $n=0$ for a relatively large q value deviates from this pattern where it also shows considerably less transient dynamics compared to other n values except for $n=3$. Therefore, in the case of larger q values, we identify smaller logarithmic perturbations ($n=1,2$) can improve transient oscillations of the donor population considerably.

4.3.2 Ohmic environments

Next we consider a donor and an acceptor pair coupled to an identical and independent Ohmic environment where the SDF is given by,

$$J_3(\omega) = q\omega_c \left(\frac{\omega}{\omega_c} \right) \exp \left(\frac{-1.1\omega}{\omega_c} \right) \left| \ln \left(\frac{\omega}{\omega_c} \right) \right|^n \quad (4.56)$$

We have obtained graphs for logarithmic power factors (n) 0 to 3 for system-bath coupling factors of (a) $q = 0.3$ (b) $q = 0.2$ (c) $q = 0.05$ and (d) $q = 0.02$. In plot (a) of Figure 4.4 where $q = 0.3$, in the case of $n=0$ and $n=1$, slight transient oscillations can be observed. For $n=1$, slightly less donor population transfer is exhibited due to the presence of low frequency modes with stronger coupling compared to the $n=0$ case as shown in Figure 4.2(b). For the higher order of logarithmic perturbations produced by $n=2$ and $n=3$, energy transfer is in the incoherent regime owing to large overall system bath couplings and large high frequency response of the corresponding SDFs. This result is significant which shows, higher order of logarithmic perturbation can cause a transfer to occur in a different regime due to its influence. Notice that for $n=2$, the steady state is achieved rapidly than for $n=3$. This is due to the relatively small low frequency response of $n=2$ makes the bath correlation function to decay rapidly compared to the $n=3$.

For plot (b) we decrease the bath coupling factor to $q = 0.2$ where $n=0$ and $n=1$ graphs appear same as in plot (a) with a slight increase of the coherent behaviour. The fact that $n=2$ and $n=3$ graphs exhibit the similar incoherent behaviour as in plot (a) is significant. In fact, $n=3$ graph in plot (b) has decayed rapidly than in plot (a), which shows the decreasing system bath coupling value has assisted the incoherent energy transfer.

In plot (c), when $n=0$, we observe the most quantum coherence effect out of all four graphs. Due to the decrease in the system bath coupling value, graph

for $n=2$ shows oscillatory dynamics and thus has been drawn into the coherent regime. Even though the initial oscillation appears very similar for $n=0,1$ and 2 , as n increases the transient oscillation reaches the steady state rapidly. Notice that even a relatively small value of $q = 0.05$, is not capable of showing quantum coherence for a larger logarithmic perturbation such as for $n=3$ due to a larger overall coupling occurred in its SDF. In the case of plot (d), all four exhibits the oscillations while for larger n values, those effects decay very promptly.

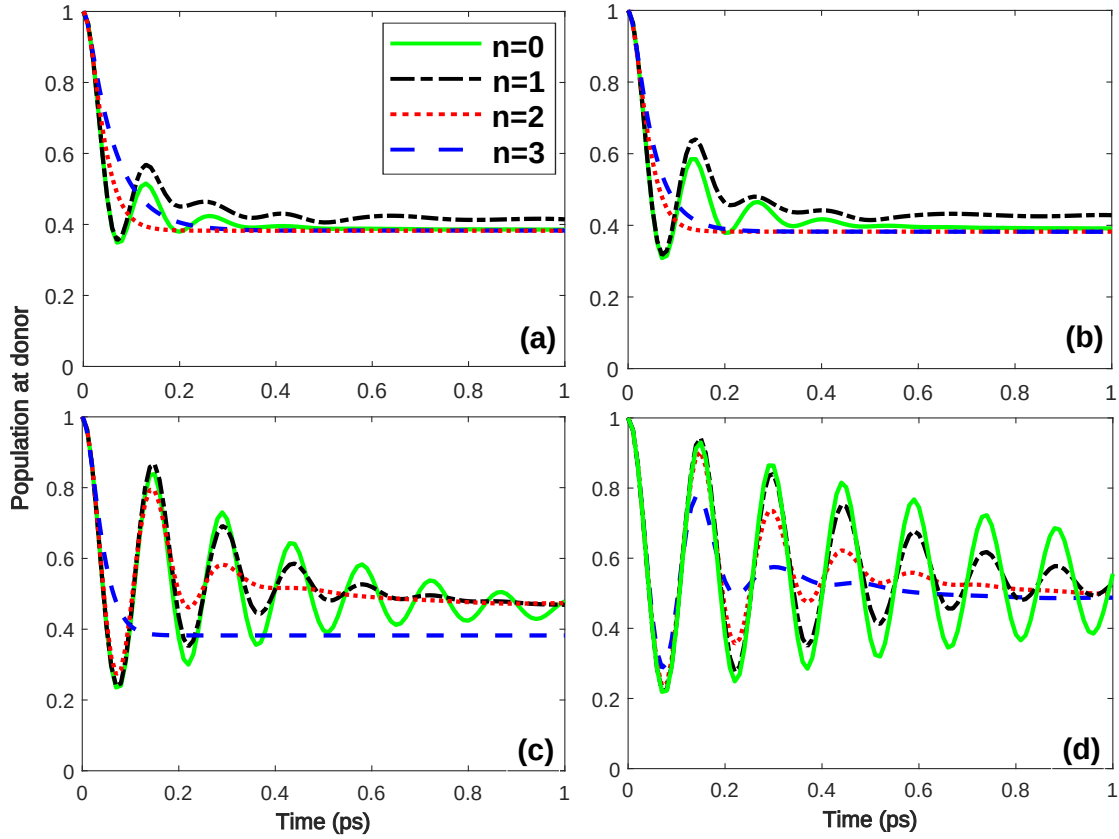


Figure 4.4: Population at donor for $J_3(\omega)$ Ohmic environment SDF with (a) $q=0.3$ (b) $q=0.2$ (c) $q=0.05$ and (d) $q=0.02$. For all cases $\alpha = 1$, $l = 1.1$, $\omega_c = 3$ THz, $\epsilon = 3$ THz, $V = 3$ THz and $T = 300$ K has been considered.

4.3.3 Effect of logarithmic perturbation on the Ohmicity parameter

In Figure 4.5 we investigate how Ohmicity parameter α effects from logarithmic perturbations. Corresponding SDF is of the form,

$$J_4(\omega) = 0.2\omega_c \left(\frac{\omega}{\omega_c}\right)^\alpha \exp\left(\frac{-1.1\omega}{\omega_c}\right) \left|\ln\left(\frac{\omega}{\omega_c}\right)\right|^n. \quad (4.57)$$

We consider α in the range of 1 (Ohmic) to 2.5 (super-Ohmic) for this experiment. In plot (a) when $n=0$, we observe coherent dynamics for all the considered environments. In plot (b) which is for the case of $n=1$, Ohmic case exhibits transient oscillatory dynamics. As for the steady state donor population, Ohmic case has a slightly higher donor population (less efficient transfer) than super-Ohmic environments for $n=1$ at 1 ps. This is due to the larger low frequency response compared to the high frequency response introduces long time correlations in the bath correlation functions. As α increases from 1 to 2, coherent dynamics are also increased where $\alpha = 2$ graph shows significant oscillations. This is due to the reduction of the overall bath coupling when α increases from 1 to 2 for $n=1$ (refer $n=1$ graphs for Figure 4.2(a), Figure 4.2(b) and Figure 4.2(c)). A gradual reduction in quantum coherence is observed as α increases from 2 to 2.5 due to increased overall bath coupling (refer $n=1$ graphs for Figure 4.2(c) and Figure 4.2(d)). When $n=2$, in plot (c), we find an incoherent transfer for the Ohmic bath where increased logarithmic perturbation factor has decreased the coupling of high frequency modes which governs the initial bath correlations. Graphs for $\alpha = 1.5, 2$ and 2.5 show similar oscillations to $n=1$ case with slight increase in the amplitude, but $\alpha = 1.5$ graph reaches a higher donor population (less efficient transfer) than super-Ohmic environments at 1 ps due to the presence of larger low frequency component out of the three.

This behaviour is consistent for $\alpha = 1.5$ graph in plot (d) even though the value

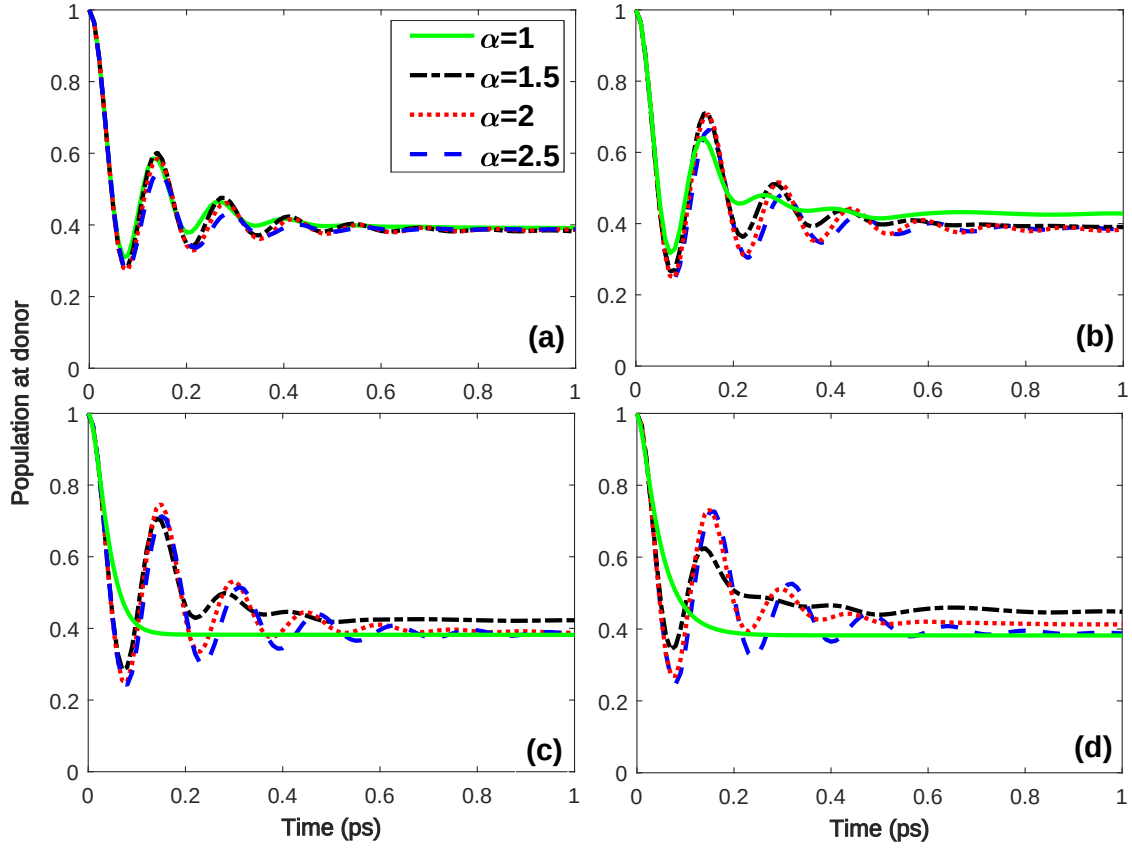


Figure 4.5: Population at donor for $J_4(\omega)$ SDF with (a) $n=0$ (b) $n=1$ (c) $n=2$ and (d) $n=3$. For all cases $q = 0.2$, $l = 1.1$, $\omega_c = 3$ THz, $\epsilon = 3$ THz, $V = 3$ THz and $T = 300$ K has been considered.

of n is increased to 3. Interesting fact to note is that, $\alpha = 1.5$ suffers from severe damping due to the increased logarithmic factor. As in plot (c), an increase in amplitude of the oscillatory behaviour can also be seen for $\alpha = 2$ and 2.5 . Notice that for Ohmic bath, incoherent transfer takes much longer time to arrive at the steady state compared to plot (c) due to the increase of the coupling strength of the low frequency modes. When comparing all four plots, we see oscillatory effects in Ohmic environments ($\alpha = 1$) are present only in the cases of $n=1$ and $n=2$. Graphs for $\alpha = 2$ and 2.5 show the most immunity to logarithmic perturbations across all the plots present in the figure which have a substantial amount of transient oscillations in each plot. Also, it is observed that larger Ohmicity val-

ues ($\alpha=2$ and 2.5) are capable of increasing coherent dynamics when logarithmic perturbations are increased.

4.4 Summary and Conclusions

In summary, we have investigated the effect of logarithmic perturbations effect on Ohmic like spectral densities using a second-order time local variational master equation. For the extensive analysis, logarithmic perturbations on the factor of bath coupling strength and the Ohmicity parameter have been considered. When the SDF defines a bath in the super-Ohmic regime, we observed that a smaller logarithmic perturbation (order of 1 and 2) can increase the quantum coherence present in the system in the region of relatively large bath coupling strengths.

In regard to the effect on Ohmicity parameter by logarithmic perturbations, we found Ohmicity values of 2 and 2.5, display the most immunity to logarithmic perturbations. Also, it takes a longer time period to achieve the steady state donor population for an energy transfer operates in the Förster regime for Ohmic environments as these perturbations are increased. Further, an increase in coherent dynamics also been observed for Ohmicity values greater than 2 as logarithmic perturbations are increased. In addition, Ohmicity value of 1.5 reached a higher donor population than super-Ohmic environments at 1 ps when logarithmic perturbations are increased.

In Ohmic environments with increasing levels of logarithmic perturbations, energy transfer tends towards the incoherent regime where most of the oscillations appear with considerable damping through the range of bath coupling strengths discussed in this chapter. Furthermore, when the transfer occurs in the Förster regime, time it takes to reach the steady state donor population also gets increased with the power of logarithmic perturbations. It is also been found that for a bath having logarithmic perturbations of the order of 1 in an Ohmic environ-

ment, can result in a less efficient energy transfer for larger system bath coupling strengths.

Aforementioned coherent transient oscillations show quantum behaviour of the excitations where excitations move back and forth (de-localized) between the donor and the acceptor (quantum coherence). Quantum coherence effects are shown to improve the efficiency of the energy transfer as shown in [13, 99, 100]. When the oscillations are strong, it takes a longer time to reach the steady state which is not ideal (less damping), whereas if the oscillations are weak to none, system loses its quantumness making the energy transfer incoherent. Therefore, quantum coherence in the right amount not only preserve the quantumness of the system but also facilitate the energy transfer. One other major advantage of quantum coherence is that it can reduce the trapped excitations in energy minima of the energy transferring paths [54].

In conclusion, the work presented here is substantial in designing realistic quantum systems in future where the SDF can be altered to facilitate more quantum coherence. In addition, avoiding such logarithmic perturbations can also be considered to preserve the available transient dynamics of such systems. In fact, increased logarithmic perturbations can be used to reduce the quantum coherence and shift the transfer into the incoherent regime for applications having such a requirement. Future research on ways that these logarithmic perturbations can be enhanced, controlled and rectified in a quantum environment will also be interesting.

Chapter 5

Performance of multi-site full polaron quantum master equation in a perturbed environment

5.1 Introduction

As the foundational piece in studying quantum systems, two-level donor-acceptor system has been utilized in a plethora of studies. Owing to the simplicity of this system, equations and calculations in such systems are easy to work with. When we extend the quantum system of interest into multiple sites, this macroscopic view introduces new challenges to the study such as complex inter site coupling and complex system bath relations. These complex equations and calculations demand a higher computational power in our hardware and they take a longer time to solve in general. Therefore, such multi-site systems are best to study using approximation methods like second-order perturbation based theories than numerically exact methods. Multi-site full polaron based quantum master equation is one such approximation method which has been used to study energy transfer dynamics of multi-site systems particularly in super-ohmic environments.

Our objective in this chapter is to analyse an interacting multi-site system attached to a perturbed super-Ohmic environment (which we simulate using logarithmic perturbations) using a multi-site full polaron transformation-based quan-

tum master equation as shown in Figure 5.1. Ensuing the introduction, in section 5.2 we outline our theory and formulate a quantum master equation. In section 5.3, we discuss the results obtained using the quantum master equation derived in the earlier section. Finally, section 5.4, summarize and concludes the chapter.

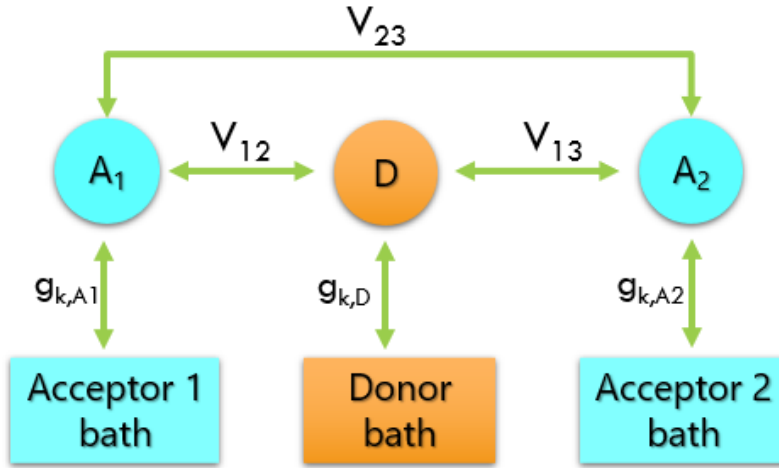


Figure 5.1: Donor chromophore (D) and two acceptor chromophores (A_1, A_2) are connected to identical and independent baths. V_{12}, V_{13}, V_{23} represents the inter-chromophore couplings whereas $g_{k,D}, g_{k,A1}, g_{k,A2}$ represents the coupling between k^{th} bath mode of each bath and the attached chromophore.

5.2 Multisite Quantum System

For our model of this analysis, we consider a system consisting three spatially-localised interacting two-level chromophores attached to individual boson environments. At $t=0$, we carefully excite the Donor chromophore (D) using an instantaneous laser pulse. Donor chromophore (D) interacts with two acceptor chromophores, A_1 and A_2 . Initial condition of the combined quantum system can be expressed as,

$$\hat{\rho}(0) = \hat{\rho}_S(0) \otimes \frac{e^{-\beta \hat{H}'_b}}{Z} \quad (5.1)$$

assuming separable states. The partition function of the bath can be written by taking the trace over bath degrees of freedom as $Z = \text{Tr}_b\{e^{-\beta\hat{H}'_b}\}$ with the assumption that bath being a canonical ensemble. Here, $\hat{H}'_b$ term represents the bath Hamiltonian and $\beta = 1/k_B T$ where k_B is the Boltzmann's constant and T is the temperature in Kelvins. In addition, initial total system sites condition is denoted by $\hat{\rho}_S(0)$.

5.2.1 Combined Hamiltonian

Combined Hamiltonian of the system and environment can be expressed as

$$\begin{aligned} \hat{H}' = \sum_n \epsilon_n |n\rangle \langle n| + \sum_{n \neq m} V_{nm} |n\rangle \langle m| + \sum_n |n\rangle \langle n| \sum_k \hbar \omega_{k,n} g_{k,n} (\hat{b}_{k,n}^\dagger + \hat{b}_{k,n}) \\ + \sum_{n,k} \hbar \omega_{k,n} \hat{b}_{k,n}^\dagger \hat{b}_{k,n} \end{aligned} \quad (5.2)$$

in the expanded form where $n = D, A_1, A_2$ throughout the chapter. First term is the population Hamiltonian where ϵ_n being the site energy of site n . Second term expresses the coherence Hamiltonian where V_{nm} denotes the site-site coupling between site n and site m . Next term denotes the system-bath Hamiltonian where $g_{k,n}$ represents the coupling strength between n^{th} site and k^{th} frequency mode in the bath which is fully characterized by the bath's spectral density function. Mode frequency of the k^{th} mode attached to n^{th} site is expressed as $\omega_{k,n}$ with corresponding creation ($\hat{b}_{k,n}^\dagger$) and annihilation ($\hat{b}_{k,n}$) bath operators. Final term represents the summation of bath Hamiltonians attached to each site.

5.2.2 Transformation into full polaron frame

When analysing the magnitudes of above Hamiltonians in various system-bath coupling regimes, we can identify that inclusion of second-order perturbation

theory in an effort to derive a consistent quantum master equation valid in all system-bath coupling regimes is not possible in the current reference frame of the Hamiltonians. This is mainly due to the fact that contribution of all Hamiltonians are significant in at least one coupling regime leaving no Hamiltonian to apply the second-order perturbation. In order to alter the current reference frame, we follow the full-polaron unitary transamination method which transforms the reference frame into the polaron frame [45,46,50]. In this polaron frame, it has been shown that contribution of system-bath Hamiltonian to the total system Hamiltonian is low at all times making it the perfect candidate to apply the second-order perturbation theory. This unitary transformation, dresses the system with bath effects which results in polaron shifted site energies and renormalized site coupling strengths. It is also important to note that application of the unitary transformation doesn't alter the physical quantum system. Now, let's consider the polaron generator function given by [43,44,58],

$$G = \sum_n |n\rangle \langle n| \sum_k \frac{g_{k,n}}{\hbar\omega_{k,n}} (\hat{b}_{k,n}^\dagger - \hat{b}_{k,n}). \quad (5.3)$$

Utilizing above function, we transform the combined system Hamiltonian through $\hat{H} = e^G \hat{H}' e^{-G}$ where we can rewrite the polaron frame combined system Hamiltonian as $\hat{H} = \hat{H}_0 + \hat{H}_1$. Here, $\hat{H}_0$ is the zeroth order Hamiltonian given by,

$$\hat{H}_0 = \sum_n \epsilon_n |n\rangle \langle n| + \sum_{n \neq m} B_n B_m V_{nm} |n\rangle \langle m| + \hat{H}'_b + \sum_n R_n \mathbb{1} \quad (5.4)$$

where,

$$B_n = \exp \left[-\frac{1}{2} \sum_k \frac{g_{k,n}^2}{\hbar^2 \omega_{k,n}^2} \coth \left(\frac{\hbar \beta \omega_{k,n}}{2} \right) \right] \quad (5.5)$$

and

$$R_n = - \sum_k \frac{g_{k,n}^2}{\hbar \omega_{k,n}}. \quad (5.6)$$

Here, $\mathbb{1}$ represents the n by n identity matrix. First order interaction Hamiltonian $\hat{H}_1$ is given by,

$$\hat{H}_1 = \sum_{n \neq m} V_{nm} \hat{B}_{nm} |n\rangle \langle m| \quad (5.7)$$

where,

$$\hat{B}_{nm} = \exp \left[\sum_k \frac{g_{k,n}}{\hbar \omega_{k,n}} (\hat{b}_{k,n}^\dagger - \hat{b}_{k,n}) - \sum_k \frac{g_{k,m}}{\hbar \omega_{k,m}} (\hat{b}_{k,m}^\dagger - \hat{b}_{k,m}) \right] - B_n B_m. \quad (5.8)$$

We can notice that in the Redfield limit, even if the magnitude of V_{nm} is large, value of $\hat{B}_{nm}$ is so small that resultant magnitude of $\hat{H}_1$ is negligible compared to the zeroth order Hamiltonian. This behaviour is also holds in the Förster limit where $\hat{B}_{nm}$ is larger and V_{nm} is smaller. Therefore, using the full polaron transformation method we have identified a Hamiltonian in $\hat{H}_1$, which can be used to apply second-order perturbation theory in an effort to formulate a consistent quantum master equation.

5.2.3 Full polaron QME derivation

Next, we define the density matrix of the combined system ($\hat{\rho}$) and quantum Liouville operator ($\mathcal{L}$) related to it through,

$$\frac{d\hat{\rho}}{dt} = -i\hat{\mathcal{L}}\hat{\rho}(t). \quad (5.9)$$

It is important to mention that all these parameters are now in the full-polaron frame. At this point, we transform the initial system condition to the same reference frame following,

$$\hat{\rho}(0) = \hat{\rho}_S(0) \otimes \left[\frac{\hat{B}_+ \exp(-\beta \hat{H}_b) \hat{B}_-}{Z} \right], \quad (5.10)$$

where,

$$\hat{B}_{\pm} = \exp \left[\sum_k \pm \frac{g_{k,n}}{\hbar \omega_{k,n}} \left(\hat{b}_{k,n}^{\dagger} - \hat{b}_{k,n} \right) \right]. \quad (5.11)$$

Subsequently, we alter all the Hamiltonians to the interaction picture and apply the second-order perturbation theory. Next step of deriving the full-polaron quantum master equation entails introducing standard projection operators to extract relevant system component from the density matrix. Thus, we define the standard projection operator method [55] denoted by $\mathcal{P}(\cdot) \equiv \hat{\rho}_b \text{Tr}_b\{\cdot\}$, which extracts the relevant part (reduced system density matrix) and the complementary projection $\mathcal{Q}(\cdot) = (I - \mathcal{P})(\cdot)$ extracts irrelevant part from the density matrix (bath). After applying the above method, resultant time-local quantum master equation can be written in the form of,

$$\frac{d\hat{\sigma}_I(t)}{dt} = \hat{\mathcal{I}}(t) - \hat{\mathcal{R}}(t)\hat{\sigma}_I(t), \quad (5.12)$$

where $\hat{\sigma}_I(t)$ denotes the time varying reduced density matrix and $\hat{\mathcal{I}}(t)$ indicates the time varying inhomogeneous term accounts for non-Markovian bath dynamics in the interaction picture. Since the contribution of the inhomogeneous term is negligible in most cases, we ignore that term from our analysis. Now, the remaining part of the quantum master equation can be written as,

$$\hat{\mathcal{R}}(t)\hat{\sigma}_I(t) = - \int_0^t d\tau \text{Tr}_b\{[\hat{H}_{1,I}(t), [\hat{H}_{1,I}(\tau), \hat{\sigma}_I(t)]]\}, \quad (5.13)$$

in the expanded form. By decomposing interaction Hamiltonian in the form of $\hat{H}_{1,I}(t) = \sum_{i=1}^6 \hat{\mathcal{Y}}_{i,I}(t) \otimes \hat{B}_{i,I}(t)$, we can simplify and write the quantum master equation in the Schrödinger picture as,

$$\frac{d\hat{\sigma}(t)}{dt} = -i [\hat{H}_S, \hat{\sigma}(t)] - \sum_{i,j} \int_0^t d\tau (\Lambda_{ij}(\tau) \{ \hat{\mathcal{Y}}_i \hat{\mathcal{Y}}_j(\tau) \hat{\sigma}(t) - \hat{\mathcal{Y}}_j(\tau) \hat{\sigma}(t) \hat{\mathcal{Y}}_i \} + h.c.) \quad (5.14)$$

where $\hat{\mathcal{Y}}_i$ denotes the system operators, $\hat{B}_i$ describes bath operators and $\Lambda_{ij}(\tau)$ expresses the bath correlation functions. System operators of the interaction Hamiltonian are given by $\mathcal{Y}_i^{xx} = |n\rangle \langle n|$ when $1 \leq i \leq 3$ and $\mathcal{Y}_i^{yy} = |n\rangle \langle m| + |m\rangle \langle n|$ when $3 < i \leq 6$. Corresponding bath correlation functions in those regimes can be written as,

$$\Lambda_{nmpq}^{xx}(t) = \frac{1}{2} V_{nm} V_{pq} B_n B_m B_p B_q \{ \exp [\delta_{np} \phi_n^{xy}(t) + \delta_{mq} \phi_m^{xy}(t)] \\ + \exp [-\delta_{np} \phi_n^{xy}(t) - \delta_{mq} \phi_m^{xy}(t)] - 2 \}$$

and

$$\Lambda_{nmpq}^{yy}(t) = \frac{1}{2} V_{nm} V_{pq} B_n B_m B_p B_q \{ \exp [\delta_{np} \phi_n^{xy}(t) + (\delta_{mq} - \delta_{mp}) \phi_m^{xy}(t)] \\ - \exp [-\delta_{np} \phi_n^{xy}(t) - (\delta_{mq} - \delta_{mp}) \phi_m^{xy}(t)] \}$$

where

$$\phi_n^{xy}(t) = \int_0^\infty d\omega \frac{J_n(\omega)}{\omega^2} [\cos(\omega t) \coth(\beta\omega/2) - i \sin(\omega t)] . \quad (5.15)$$

Here, δ_{nm} are Kronecker delta operators and $J_n(\omega)$ is the spectral density function of the bath attached to n^{th} site.

5.2.4 Disturbed super ohmic environments

Our goal in this chapter is to examine the coherent energy transfer dynamics of a multisite quantum system through full-polaron transformation based quantum master equation where the attached quantum super ohmic environments are slightly disturbed/perturbed in the frequency domain. This disturbance can be simulated using a novel type of spectral density function given by,

$$J(\omega) = q\omega_c \left(\frac{\omega}{\omega_c} \right)^\alpha \exp \left(\frac{-l\omega}{\omega_c} \right) \left| \ln \left(\frac{\omega}{\omega_c} \right) \right|^n . \quad (5.16)$$

as shown in previous chapters. Figure 5.2 shows the behaviour of the function against the frequency measured in THz.

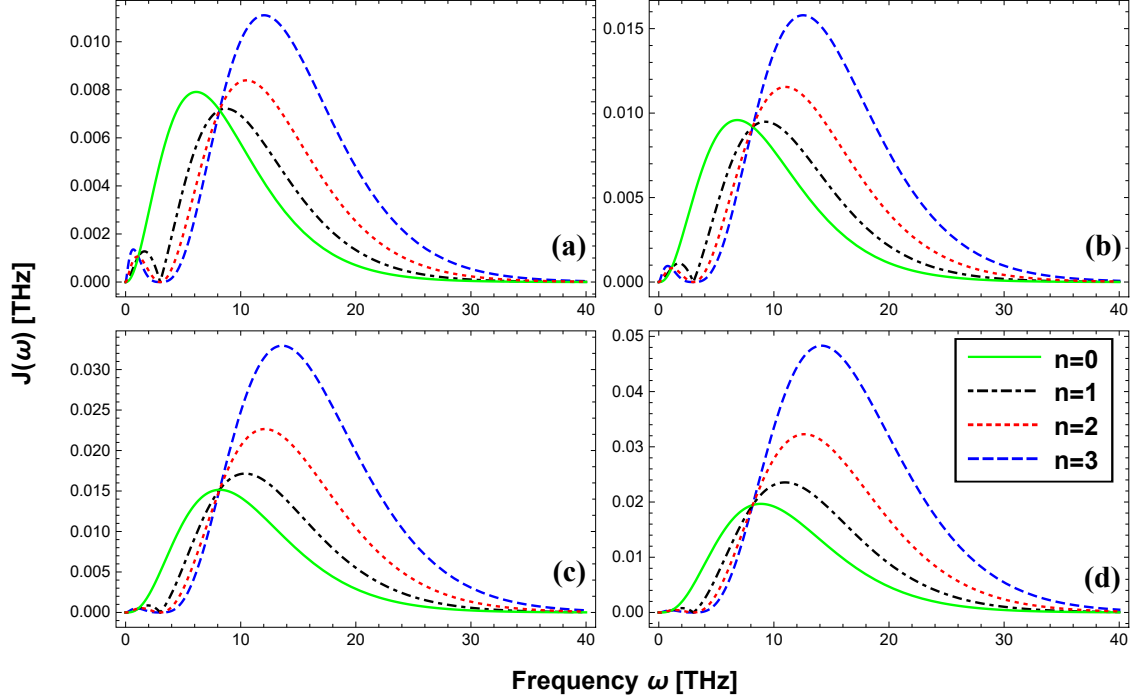


Figure 5.2: Spectral density functions of $J(\omega)$ for the values of (a) $\alpha=2.25$, (b) $\alpha=2.5$, (c) $\alpha=3$, (d) $\alpha=3.25$. Values of n are shown on the graphs. For each case we take $\omega_c = 3$ THz, $l=1.1$ and $q=0.005$.

5.3 Results and Discussion

Utilizing derived Eq. (5.14), we can extract the population of sites (where $n = D, A_1, A_2$) using,

$$P_n(t) = \langle n | \hat{\sigma}(t) | n \rangle. \quad (5.17)$$

Despite the fact that $\hat{\sigma}(t)$ term is in the full-polaron frame, the extracted populations are of the same magnitude in the original frame. This is due to the fact that population Hamiltonian doesn't rely on bath creation and annihilation operators, $e^G |n\rangle \langle n| e^{-G} = |n\rangle \langle n|$ [43–45, 58, 101]. Ensuing sections illustrate the population

dynamics we obtained for different super-Ohmic environments.

5.3.1 Performance in different system-bath coupling regimes

In this section, we examine the performance of full polaron transformation-based multi-site quantum master equation in various system-bath coupling regimes. For our analysis, we have selected $\alpha = 3$, $l = 1.1$, $\omega_c = 3$ THz, $V_{13} = 0$, $\epsilon_1 = \epsilon_2 = 1.5$ THz, $\epsilon_3 = 0$ and $T = 300$ K. We have considered the population dynamics in the intermediate coupling regime ((a) $q = 0.1$, $V_{12} = V_{23} = 0.6$ THz), in the Redfield limit ((b) $q = 0.01$, $V_{12} = 6$ THz, $V_{23} = 3$ THz) and near the Förster limit ((c) $q = 0.2$, $V_{12} = 9$ THz, $V_{23} = 3$ THz) as shown in Figure 5.3. Corresponding spectral density function is given by,

$$J_2(\omega) = q\omega_c \left(\frac{\omega}{\omega_c}\right)^3 \exp\left(\frac{-1.1\omega}{\omega_c}\right) \left|\ln\left(\frac{\omega}{\omega_c}\right)\right|^n. \quad (5.18)$$

In the intermediate coupling regime as shown in Figure 5.3(a), We observe that $n=0$ graph shows the most coherent dynamics out of all four graphs. When we increment the logarithmic perturbation factor(n), we see that oscillatory dynamics get reduced where $n=3$ graph shows an incoherent transfer compared to other graphs. Here, it is important to note that, higher order of logarithmic perturbations are capable of forcing the population dynamics to occur in the incoherent regime. When observing A_1 and A_2 populations, it is evident that coherent dynamics have transferred from one site to the other.

We notice that when the combined system operates in the Redfield limit, the presence of strong oscillations compared to other regimes. This is mainly owing to the fact that system sites are coupled strongly compared to the system-bath coupling strength which reduces the bath's influence on the sites. As in the case of Figure 5.3(a), in Figure 5.3(b) we identify that $n=0$ graph reveals quantum coherent effects more than other graphs. In addition, as in the previous case

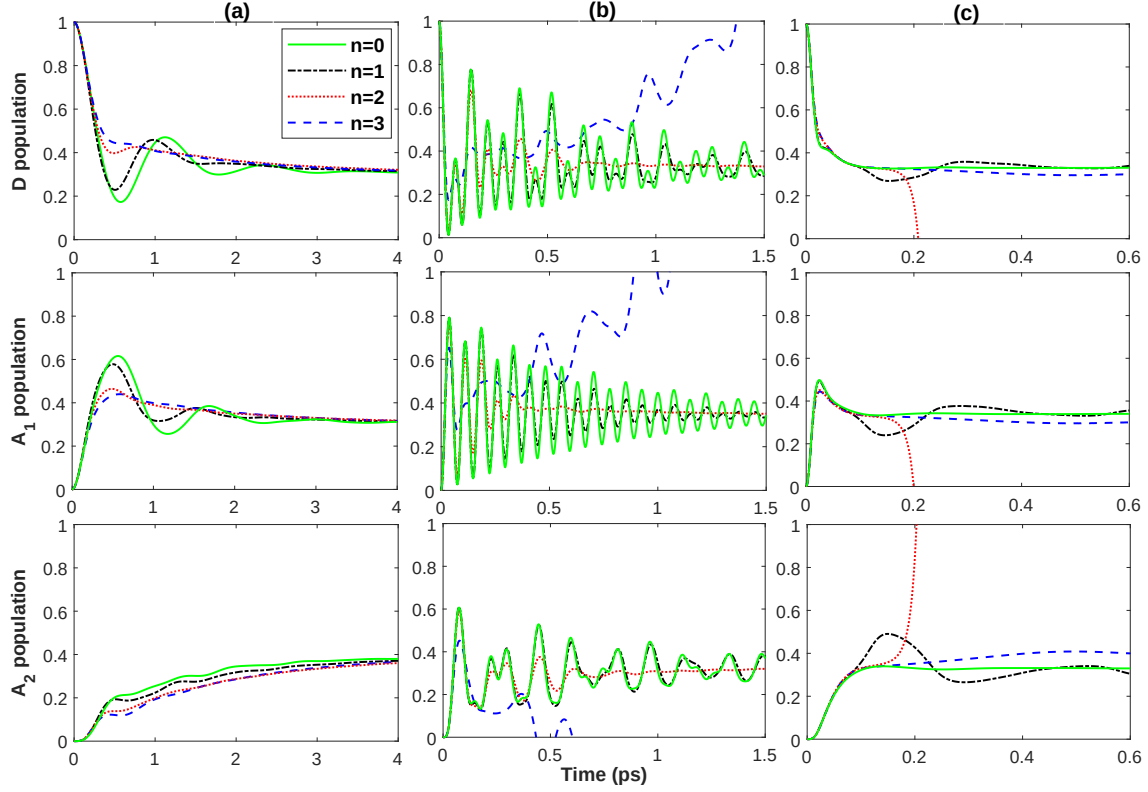


Figure 5.3: Population at donor (D), acceptor 1 (A_1) and acceptor 2 (A_2) for $J_2(\omega)$ SDF with (a) $q = 0.1$, $V_{12} = V_{23} = 0.6$ THz (b) $q = 0.01$, $V_{12} = 6$ THz, $V_{23} = 3$ THz and (c) $q = 0.2$, $V_{12} = 9$ THz, $V_{23} = 3$ THz. For all cases $\alpha = 3$, $l = 1.1$, $\omega_c = 3$ THz, $\epsilon_1 = \epsilon_2 = 1.5$ THz, $\epsilon_3 = 0$, $V_{13} = 0$, $\hbar = 1$ and $T = 300$ K has been considered.

we observe a similar behaviour of larger logarithmic perturbation factors having larger implications on the oscillatory dynamics of the site populations. In fact, even-though both $n=0$ and $n=1$ graphs reveal similarities in their dynamics, we identify that $n=2$ graph entails a rapid decay in the coherent behaviour. When the logarithmic factor is increased to 4, full polaron based multi-site quantum master equation has suffered infrared divergence effect. Therefore, we can corroborate the fact that larger logarithmic factors in Redfield limit can restrict the use of this quantum master equation to simulate population dynamics. In the Förster limit as shown in Figure 5.3(c), we observe severe distortions in the graphs of $n=1$, $n=2$ and $n=3$. This is due to the fact that when system-bath coupling is larger

compared to coupling among the sites, bath influence plays a major role in the population dynamics. According to Figure 5.2, we can observe that larger logarithmic perturbations entail smaller low frequency responses which affect both short term and long term dynamics. This smaller low frequency response has resulted in revealing infrared divergence effect in population dynamics in donor and both acceptors due to divergence transpires in the bath correlation function. When there are no logarithmic perturbations, $n=0$ graph has indicated an incoherent transfer.

Therefore, we can corroborate the fact that full polaron transformation based multi-site quantum master equation reveals coherent resonance energy transfer dynamics in both Redfield limit and intermediate coupling regime. It is evident that higher logarithmic perturbations have a larger influence on the oscillatory dynamics where we observe either smaller or no oscillations when the n value is larger. In addition, in Redfield limit and Förster limit, we illustrated the occurrence of infrared divergence effect when these perturbations are present. It is also important to mention that, coupling between sites plays a major role in observed coherent oscillations. This is evident when examining Figure 5.3(a) and Figure 5.3(b), where the coupling between donor (D) chromophore and acceptor 1 (A_1) chromophore is large compared to coupling between acceptor 1 (A_1) chromophore and acceptor 2 (A_2) chromophore. Here, we identify acceptor 1 (A_1) chromophore indicates large oscillations which can be compared to donor (D) chromophore whereas acceptor 2 (A_2) chromophore has minor oscillations.

5.3.2 Performance in various Ohmicity values

We analyse the performance of the derived quantum master equation in various super-Ohmic environments in this section. Figure 5.4 is obtained for the values of $q = 0.05$, $l = 1.1$, $\omega_c = 3$ THz, $\epsilon_1 = \epsilon_2 = 1.5$ THz, $\epsilon_3 = 0$, $q = 0.2$, $V_{12} = 6$

92 THz, $V_{23} = 3$ THz, $V_{13} = 0$ and $T = 300$ K where scenario (a) $n=1$, (b) $n=2$ and (c) $n=3$. We examine the super-Ohmic environments with Ohmicity values $\alpha = 2.5$, $\alpha = 3$, $\alpha = 3.5$ and $\alpha = 4$. Considered spectral density function can be written as,

$$J_3(\omega) = 0.05\omega_c \left(\frac{\omega}{\omega_c}\right)^\alpha \exp\left(\frac{-1.1\omega}{\omega_c}\right) \left|\ln\left(\frac{\omega}{\omega_c}\right)\right|^n. \quad (5.19)$$

When $n=1$ as illustrated in Figure 5.4(a), we identify that while $\alpha = 3$, $\alpha = 3.5$, $\alpha = 4$ graphs indicate coherent energy transfer dynamics, $\alpha = 2.5$ graph has shown infrared divergence effect. This is due to the fact that smaller Ohmicity value has a smaller overall coupling value compared to larger Ohmicity values. This makes them vulnerable even for smaller logarithmic perturbations where the reduction in the coupling strength of low frequency bath modes affects the bath correlation function. It is also noticeable the fact that higher Ohmicity values simulate higher oscillatory dynamics.

As we increment the value of n to $n=2$ in Figure 5.4(b), we observe that both $\alpha = 2.5$ graph and $\alpha = 3$ graph indicate infrared divergence effects. This conveys the fact that even a higher Ohmicity value such as $\alpha = 3$ is not sufficient to overcome the turbulence introduced by these logarithmic factors. Neither $\alpha = 3.5$ graph nor $\alpha = 4$ graph have affected where they display coherent dynamics in all three site populations. In Figure 5.4(c), we observe not only $\alpha = 2.5$ and $\alpha = 3$ graphs but also $\alpha = 3.5$ graph is now indicating severe distortions. In fact, $\alpha = 4$ graph is the only scenario capable of withstanding distortions when logarithmic perturbation factor is 3.

Therefore, the utilization of multi-site full polaron transformation-based quantum master equation in simulating population dynamics has to be approached with caution. As delineated earlier, the infrared divergence effect manifested in different super-Ohmic environments under various logarithmic perturbation factors make this theory to be unreliable in certain instances. In such scenarios, application of this theory will lead to inaccurate results. On a separate note, when

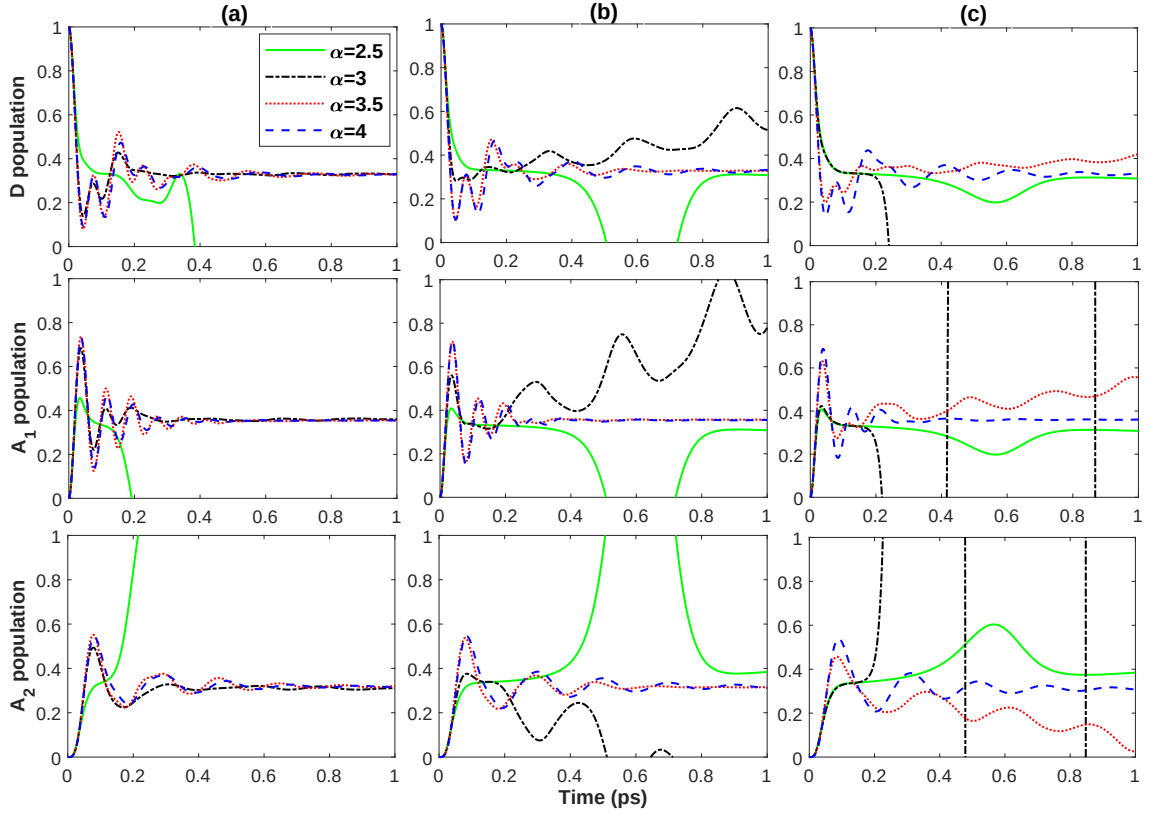


Figure 5.4: Population at donor (D), acceptor 1 (A_1) and acceptor 2 (A_2) for $J_3(\omega)$ SDF with (a) $n=1$, (b) $n=2$ and (c) $n=3$. For all cases $q = 0.05$, $l = 1.1$, $\omega_c = 3$ THz, $\epsilon_1 = \epsilon_2 = 1.5$ THz, $\epsilon_3 = 0$, $V_{12} = 6$ THz, $V_{23} = 3$ THz, $V_{13} = 0$, $\hbar = 1$ and $T = 300$ K has been considered.

we compare all three graphs, we can identify the fact that larger logarithmic factors can reduce the frequency of coherent oscillations.

5.4 Summary and Conclusions

In summary, we have formulated a full polaron transformation-based quantum master equation that can be applied to multi-site systems. Subsequently, we examined the population transfer dynamics of a three site quantum system attached to a few super-Ohmic environments which undergo logarithmic perturbations. This is achieved using a novel spectral density function, which utilizes logarithmic

mic factors entail in low frequency power series expansion of the spectral density. We have not only simulated the coherent energy transfer dynamics of this site populations but also have gauge the performance of the multi-site full polaron quantum master equation.

While we discovered this equation reveals quantum oscillatory dynamics well in Redfield limit when logarithmic perturbations are small, the performance near Förster limit was suboptimal due to the presence of infrared divergence effects even for small logarithmic perturbations. When we compare the results, we can identify that this quantum master equation performs sufficiently well in the intermediate coupling regime with logarithmic perturbations in the environment. Our results indicate that higher logarithmic perturbation factors manifest larger damping to these coherent dynamics.

Next, we examined the impact on the Ohmicity parameter when these logarithmic factors are present. Here, we corroborated the fact that higher logarithmic perturbations have decreased the frequency of quantum oscillations in the energy transfer dynamics irrespective of the magnitude of Ohmicity parameter. We also discovered the fact that larger Ohmicity values are immune to logarithmic perturbations when predicted through full polaron transformation-based multi-site quantum master equation. In addition, smaller Ohmicity values have shown infrared divergence effect even for small perturbations.

In conclusion, through this study we have identified that multi-site full polaron transformation-based quantum master equation is vulnerable for logarithmic perturbations in quantum environments. Despite the fact that, full-polaron based quantum master equations perform well in super-Ohmic environments, simulated results manifest severe distortions when super-Ohmic environments are perturbed with logarithmic factors. This study aids in deciding when to use this quantum master equation and when it is not reliable.

Chapter 6

Coherent Resonance Energy Transfer in a multi exciton transport system under logarithmic perturbations using variational polaron approach

6.1 Introduction

Most second-order perturbation formalisms based on polaron transformation techniques have a multichromophoric counterpart to two-level based theories [44,50]. These multichromophoric theories provide an insight into the experimental data gathered, such as the analysis performed on Fenna–Matthews–Olsen complex (FMO) illustrated in [44]. These theories are fundamental in understanding how energy is transferred from site to site in the energy transferring paths of the light harvesting complexes. In an effort to analyse the energy transfer of multichromophoric systems in this chapter, we have chosen variational polaron transformation based multi-exciton theory which has performed considerably in sub-Ohmic, Ohmic and super-Ohmic environments for both fast and slow baths as corroborated in [58].

In most instances found in literature, the energy transfer process is studied against the most common type of Ohmic-like SDFs consisting of an exponential decay term, where the type of the environment (whether it is sub-Ohmic, Ohmic,

or super-Ohmic) is determined by the Ohmicity parameter [43–45,69,70].

Our objectives in this chapter, are to investigate the energy transfer of a multichromophoric system in an Ohmic-like environment undergoing negative logarithmic perturbations and to compare the full polaron theory and the variational polaron theory to determine which theory is more suitable in characterizing and simulating quantum coherence behaviour of the energy transfer in these types of environments using the quantum system given in Figure 6.1.

This chapter is outlined as follows. Ensuing the introduction, in section 6.2, the formalism which includes the analytical approach deployed for our analysis is outlined. The results are discussed in section 6.3 and section 6.4 summarizes and concludes the chapter.

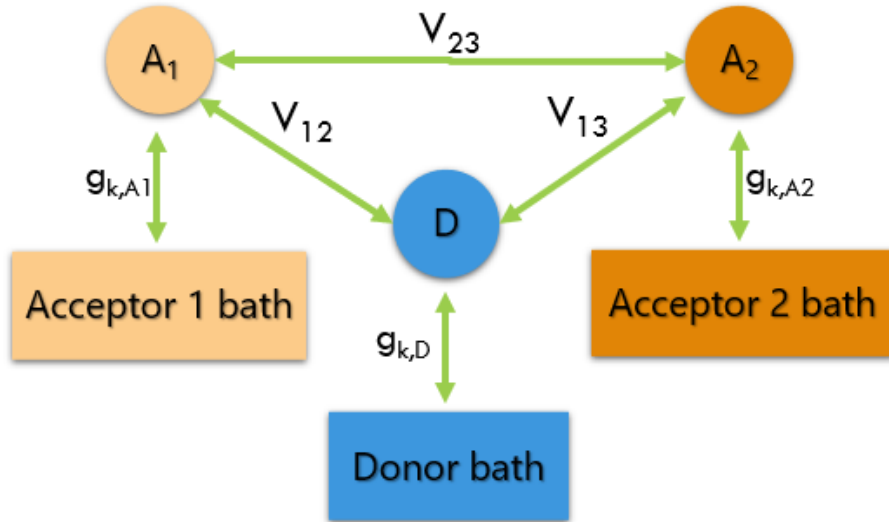


Figure 6.1: Donor chromophore (D) and two acceptor chromophores (A_1, A_2) are connected to identical and independent baths. V_{12}, V_{13}, V_{23} represents the inter-chromophore couplings whereas $g_{k,D}, g_{k,A1}, g_{k,A2}$ represents the coupling between k^{th} bath mode of each bath and the attached chromophore.

6.2 Formalism

Suppose a system with three spatially-localised interacting two-level systems surrounded by a bosonic environment. Initially, the combined density matrix of the system and the environment can be written as [102],

$$\hat{\rho}(0) = \hat{\rho}_S(0) \otimes \frac{e^{-\beta \hat{H}'_b}}{Z} \quad (6.1)$$

assuming separable states. Let's assume the bath to be a canonical ensemble and therefore, the partition function can be written as $Z = \text{Tr}_b \{e^{-\beta \hat{H}'_b}\}$ by taking the trace over bath degrees of freedom where $\hat{H}'_b$ defines the bath Hamiltonian. Here, the term $\beta = 1/k_B T$ where k_B is the Boltzmann's constant and T is the temperature of the combined system in Kelvins.

6.2.1 Combined Hamiltonian

Let's write the combined Hamiltonian of the system and environment as,

$$\hat{H}' = \hat{H}'_p + \hat{H}'_c + \hat{H}'_{sb} + \hat{H}'_b. \quad (6.2)$$

The population Hamiltonian is given by $\hat{H}'_p = \sum_n \epsilon_n |n\rangle \langle n|$ where n represents sites: Donor (D), Acceptor 1 (A_1) and Acceptor 2 (A_2) throughout the chapter. Term ϵ_n represents the localized site energy at n^{th} site. Hamiltonian of the coherences of the system is given by $\hat{H}'_c = \sum_{n \neq m} V_{nm} |n\rangle \langle m|$ where V_{nm} represents the electronic coupling strength between site n and site m . System-bath Hamiltonian is given by $\hat{H}'_{sb} = \sum_n |n\rangle \langle n| \sum_k \hbar \omega_{k,n} g_{k,n} (\hat{b}_{k,n}^\dagger + \hat{b}_{k,n})$ assuming there are no bath correlations and all system-bath coupling terms $g_{k,n}$ are real quantities which are characterized by the spectral density function. Term $\hat{b}_{k,n} (\hat{b}_{k,n}^\dagger)$ defined here, is the annihilation (creation) bath operator coupled to n^{th} site of k^{th} bath mode where

$\omega_{k,n}$ denotes the frequency of k^{th} bath mode linked to n^{th} site. Final term is the bath Hamiltonian given by $\hat{H}'_b = \sum_n \sum_k \hbar \omega_{k,n} \hat{b}_{k,n}^\dagger \hat{b}_{k,n}$. Hence, combined Hamiltonian can be written as,

$$\begin{aligned} \hat{H}' = \sum_n \epsilon_n |n\rangle \langle n| + \sum_{n \neq m} V_{nm} |n\rangle \langle m| + \sum_n |n\rangle \langle n| \sum_k \hbar \omega_{k,n} g_{k,n} (\hat{b}_{k,n}^\dagger + \hat{b}_{k,n}) \\ + \sum_{n,k} \hbar \omega_{k,n} \hat{b}_{k,n}^\dagger \hat{b}_{k,n}. \end{aligned} \quad (6.3)$$

in the expanded form.

6.2.2 Variational Polaron Transformation

Now, let us consider the polaron generator function given by [43,44,58],

$$G = \sum_n |n\rangle \langle n| \sum_k \frac{f_{k,n}}{\hbar \omega_{k,n}} (\hat{b}_{k,n}^\dagger - \hat{b}_{k,n}) \quad (6.4)$$

where the variational parameter $f_{k,n}$ is in the range of $0 \leq f_{k,n} \leq g_{k,n}$ and is a real value. Now, we transform the combined system Hamiltonian using $\hat{H} = e^G \hat{H}' e^{-G}$. Transformed Hamiltonian $\hat{H}$ can be written as a summation of the zeroth order Hamiltonian $\hat{H}_0$ and first order interaction Hamiltonian $\hat{H}_1$. Zeroth order Hamiltonian is given by,

$$\hat{H}_0 = \sum_n \epsilon_n |n\rangle \langle n| + \sum_{n \neq m} B_n B_m V_{nm} |n\rangle \langle m| + \hat{H}'_b + \sum_n R_n \mathbb{1} \quad (6.5)$$

where,

$$B_n = \exp \left[-\frac{1}{2} \sum_k \frac{f_{k,n}^2}{\hbar^2 \omega_{k,n}^2} \coth \left(\frac{\hbar \beta \omega_{k,n}}{2} \right) \right] \quad (6.6)$$

is the expected value of the bath displacement operator of the n^{th} site and $\mathbb{1}$ represents the $n \times n$ identity matrix. Polaron shift in the site energy can be written

as,

$$R_n = \sum_k \frac{f_{k,n}}{\hbar\omega_{k,n}} (f_{k,n} - 2g_{k,n}). \quad (6.7)$$

First order interaction Hamiltonian is given by,

$$\hat{H}_1 = \sum_n |n\rangle \langle n| \sum_k (g_{k,n} - f_{k,n}) (\hat{b}_{k,n}^\dagger + \hat{b}_{k,n}) + \sum_{n \neq m} V_{nm} B_{nm} |n\rangle \langle m| \quad (6.8)$$

where,

$$\hat{B}_{nm} = \exp \left[\sum_k \frac{f_{k,n}}{\hbar\omega_{k,n}} (\hat{b}_{k,n}^\dagger - \hat{b}_{k,n}) - \sum_k \frac{f_{k,m}}{\hbar\omega_{k,m}} (\hat{b}_{k,m}^\dagger - \hat{b}_{k,m}) \right] - B_n B_m \quad (6.9)$$

is the off-diagonal bath displacement operator between n^{th} site and the m^{th} site.

6.2.3 Determining the variational parameter

As elucidated before, the variational parameter $f_{k,n}$ appears in above equations, is in the range of $0 \leq f_{k,n} \leq g_{k,n}$. In order to solve the quantum master equation we need to find an exact value for this parameter within the range of $0 \leq f_{k,n} \leq g_{k,n}$. To do that, we use the Feynman-Bogoliubov upper bound on the free energy [59] as shown in [43,44]. This bound is given by,

$$A_{\text{FB}} = -\frac{1}{\beta} \ln \left[\text{Tr} \left\{ e^{-\beta \hat{H}_0} \right\} \right] + \langle \hat{H}_1 \rangle_{\hat{H}_0} + O \left(\langle \hat{H}_1^2 \rangle_{\hat{H}_0} \right). \quad (6.10)$$

Recently an improved expression for the free energy minimization argument has been introduced in [60]. Since this is the upper bound of the free energy (A), we can write $A_{\text{FB}} \geq A$. Notice that the second term in Eq. (6.10) is zero by construction and the final term can be negligible when we neglect the higher order terms of the interaction Hamiltonian. To minimize the upper bound on the

free energy consider the derivative,

$$\frac{\partial A_{\text{FB}}}{\partial f_{n,k}} = \frac{\partial A_{\text{FB}}}{\partial R_n} \frac{\partial R_n}{\partial f_{n,k}} + \frac{\partial A_{\text{FB}}}{\partial B_n} \frac{\partial B_n}{\partial f_{n,k}} = 0. \quad (6.11)$$

Next, we find the solution to the above equation as,

$$F_n(\omega_{n,k}) = \left[1 + \frac{2V_{nm}^2 B_{nm}^2}{\eta \hbar \omega_{n,k}} \tanh\left(\frac{\beta \eta}{2}\right) \coth\left(\frac{\hbar \beta \omega_{n,k}}{2}\right) \right] \quad (6.12)$$

when $f_{n,k} = g_{n,k} F_n(\omega_{n,k})$. For the purpose of formulating the quantum master equation we assume a continuous bath and therefore we write,

$$B_n = \exp \left[-\frac{1}{2} \int_0^\infty d\omega \frac{F_n(\omega_n)^2 J_n(\omega)}{\omega^2} \coth\left(\frac{\hbar \beta \omega}{2}\right) \right] \quad (6.13)$$

and

$$R_n = \int_0^\infty d\omega \frac{J_n(\omega)}{\omega} (F_n(\omega_n) - 2) F_n(\omega_n) \quad (6.14)$$

where $J_n(\omega)$ is the spectral density function attached to the n^{th} site.

6.2.4 Formulating the quantum master equation

As the first step in formulating the quantum master equation, we define the standard projection operator method [55] defined by $\mathcal{P}(\cdot) \equiv \hat{\rho}_b \text{Tr}_b\{\cdot\}$ which extracts the system part of the density matrix and the complimentary projection $\mathcal{Q}(\cdot) = (I - \mathcal{P})(\cdot)$ extracts the irrelevant part of the density matrix which is the bath. Next, we define the quantum Liouville operators which governs the time evolution of the density matrix as shown in Eq. (6.15) in an effort to develop a time-local second-order quantum master equation for our analysis,

$$\frac{d\hat{\rho}}{dt} = -i\hat{\mathcal{L}}\hat{\rho}(t). \quad (6.15)$$

Next, we transform the initial condition given in Eq. (6.1) of the combined system into the variational polaron frame through,

$$\hat{\rho}(0) = \hat{\rho}_S(0) \otimes \left[\frac{\hat{B}_+ \exp(-\beta \hat{H}_b) \hat{B}_-}{Z} \right], \quad (6.16)$$

where,

$$\hat{B}_{\pm} = \exp \left[\sum_k \pm \frac{f_{k,n}}{\hbar \omega_{k,n}} \left(\hat{b}_{k,n}^{\dagger} - \hat{b}_{k,n} \right) \right]. \quad (6.17)$$

Subsequently, we transform the Hamiltonians into the interaction picture and apply the second-order perturbation theory to the variational polaron transformed system-bath Hamiltonian. The resultant quantum master equation can be expressed in the form of,

$$\frac{d\hat{\sigma}_I(t)}{dt} = \hat{\mathcal{I}}(t) - \hat{\mathcal{R}}(t)\hat{\sigma}_I(t), \quad (6.18)$$

where,

$$\hat{\mathcal{R}}(t)\hat{\sigma}_I(t) = - \int_0^t d\tau \text{Tr}_b \{ [\hat{H}_{1,I}(t), [\hat{H}_{1,I}(\tau), \hat{\sigma}_I(t)]] \}. \quad (6.19)$$

Here, $\hat{H}_{1,I}(t)$ is the interaction picture zero-order Hamiltonian and $\hat{\sigma}_I(t)$ is the interaction picture reduced system density matrix. At this point we ignore the contribution of time varying inhomogeneous term $\hat{\mathcal{I}}(t)$ which accounts for non-Markovian bath dynamics in the interaction picture since it is negligible compared to the homogeneous term $\hat{\mathcal{R}}(t)$. Also, note that we can decompose $\hat{H}_{1,I}(t)$ as, $\hat{H}_{1,I}(t) = \sum_{i=1}^9 \hat{\mathcal{Y}}_{i,I}(t) \otimes \hat{B}_{i,I}(t)$ where $\hat{\mathcal{Y}}_i$ expresses the interaction picture system operators and $\hat{B}_{i,I}$ describes interaction picture bath operators. Applying this decomposition we derive a quantum master equation in the Schrödinger picture

which is given by,

$$\frac{d\hat{\sigma}(t)}{dt} = -i [\hat{H}_S, \hat{\sigma}(t)] - \sum_{i,j} \int_0^t d\tau (\Lambda_{ij}(\tau) \{ \mathcal{Y}_i \mathcal{Y}_j(\tau) \hat{\sigma}(t) - \mathcal{Y}_j(\tau) \hat{\sigma}(t) \mathcal{Y}_i \} + h.c.) \quad (6.20)$$

where $\Lambda_{ij}(\tau)$ denotes the bath correlation functions. System operators of the interaction Hamiltonian are given by $\mathcal{Y}_i^{xx} = |n\rangle \langle n|$ when $1 \leq i \leq 3$, $\mathcal{Y}_i^{yy} = |n\rangle \langle m| + |m\rangle \langle n|$ when $3 < i \leq 6$ and $\mathcal{Y}_i^{zz} = i |n\rangle \langle m| - i |m\rangle \langle n|$ when $6 < i \leq 9$. Corresponding bath correlation functions in those regimes can be written as,

$$\Lambda_n^{zz}(t) = \int_0^\infty d\omega J_n(\omega) [1 - F_n(\omega)]^2 [\cos(\omega t) \coth(\beta\omega/2) - i \sin(\omega t)] ,$$

$$\Lambda_{nmpq}^{xx}(t) = \frac{1}{2} V_{nm} V_{pq} B_n B_m B_p B_q \{ \exp[\delta_{np} \phi_n^{xy}(t) + \delta_{mq} \phi_m^{xy}(t)] + \exp[-\delta_{np} \phi_n^{xy}(t) - \delta_{mq} \phi_m^{xy}(t)] - 2 \}$$

and

$$\Lambda_{nmpq}^{yy}(t) = \frac{1}{2} V_{nm} V_{pq} B_n B_m B_p B_q \{ \exp[\delta_{np} \phi_n^{xy}(t) + (\delta_{mq} - \delta_{mp}) \phi_m^{xy}(t)] - \exp[-\delta_{np} \phi_n^{xy}(t) - (\delta_{mq} - \delta_{mp}) \phi_m^{xy}(t)] \}$$

where

$$\phi_n^{xy}(t) = \int_0^\infty d\omega \frac{J_n(\omega)}{\omega^2} F_n^2(\omega) [\cos(\omega t) \coth(\beta\omega/2) - i \sin(\omega t)] . \quad (6.21)$$

We define δ_{nm} to be Kronecker delta operators between site n and m and $J_n(\omega)$ is the spectral density function of the bath attached to n^{th} site. Final bath correlation function is the cross interaction term given by,

$$\Lambda_{nmpq}^{yz}(t) = \delta_{np} V_{nm} B_n B_m \phi_n^{yz}(t) \quad (6.22)$$

where

$$\phi_n^{yz}(t) = \int_0^\infty d\omega \frac{J_n(\omega)}{\omega} [1 - F_n(\omega)] F_n(\omega) [\sin(\omega t) \coth(\beta\omega/2) + i \cos(\omega t)] . \quad (6.23)$$

6.2.5 Perturbed environments

Our objective is to study the multi-exciton energy transport in an environment where the spectral density function is slightly deviated from original form. In order to deviate the spectral density function from its original form, we need to perturb it by combining it with another factor which its nature is different from the exponential decay. For that purpose, logarithmic factors are used to perturb the most common type of spectral density functions. In doing so, we can come up with an Ohmic-like spectral density function which experience logarithmic perturbations as [51,101],

$$J(\omega) = q\omega_c \left(\frac{\omega}{\omega_c}\right)^\alpha \exp\left(\frac{-l\omega}{\omega_c}\right) \left|\ln\left(\frac{\omega}{\omega_c}\right)\right|^n \quad (6.24)$$

where l is the factor of the exponential decay and n is the power of the logarithmic factor as elucidated before in previous chapters. In fact, this form of Ohmic-like SDF experiencing logarithmic perturbations subsumes low frequency power-law profiles obtained by removable logarithmic singularities. Besides, it has been shown that this form of SDFs can be used to interpret a large range of relaxations which are slower than the exponential decay and faster or slower than the inverse power laws in quantum systems [51].

In an effort to visualize the shape of the spectral density functions we have plotted Figure 6.2. When observing the graphs, we can identify for each value of α , all the $J_{\alpha,n}$ functions intersect at $\omega = \omega_c/e$ and at $\omega = \omega_c e$. These intersections

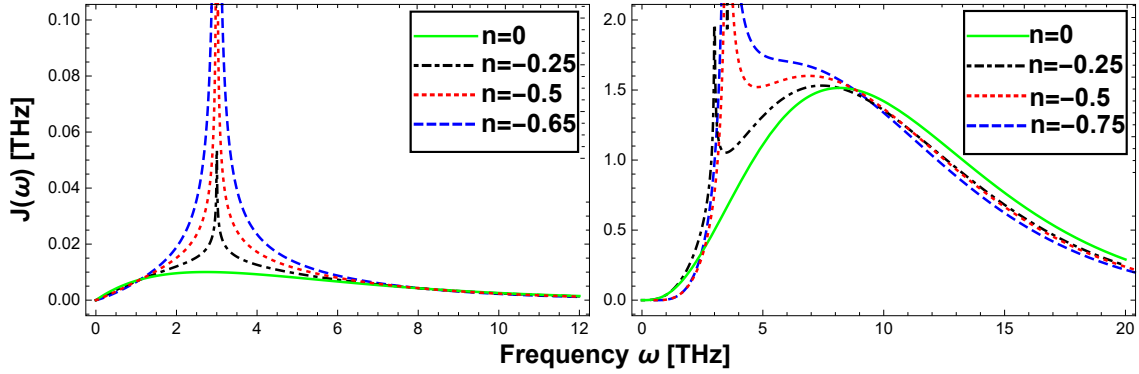


Figure 6.2: Spectral density functions of $J(\omega)$ for the values of (a) $\alpha=1, q=0.01$ and (b) $\alpha=3, q=0.5$. Values of n are shown on the graphs. For each case we take $\omega_c = 3$ THz and $l=1.1$.

divide the frequency space into three regions.

- The low-frequency range $(0, \omega_c/e)$, in which $J_{\alpha, n_1} < J_{\alpha, n_2}$ for all $n_1 < n_2$.
- The intermediate range $(\omega_c/e, \omega_c e)$, in which $J_{\alpha, n_1} < J_{\alpha, n_2}$ for all $n_1 > n_2$.
- The high-frequency range $(\omega_c e, \infty)$, in which $J_{\alpha, n_1} < J_{\alpha, n_2}$ for all $n_1 < n_2$.

We can identify the fact that, in the intermediate region, area under the curves are decreasing as we increase the logarithmic power factor n from -0.75 to 0 . In the remaining low frequency region and the high-frequency region, we see the opposite effect is true where $n=0$ graph has the largest area. As the area under these curves represents the total coupling to the attached sites, we can see increased influences from the bath modes in the intermediate region to the energy transfer. This is due to the lesser contribution from low-frequency bath modes and the high frequency bath modes to the overall coupling.

6.3 Results and Discussion

Now, let's analyse how these logarithmic perturbations can alter energy transfer dynamics in super Ohmic and Ohmic environments. First, we need to find the donor population, 1st acceptor population and the 2nd acceptor population by

solving Eq. (6.20) and extracting the site population using,

$$P_n(t) = \langle n | \hat{\sigma}(t) | n \rangle \quad (6.25)$$

where $n = D, A_1, A_2$. It is also important to mention that, even-though $\hat{\sigma}(t)$ term is in the polaron transformed frame, site population extracted using above formula represents the accurate site population in the original frame. This is due to population Hamiltonian being independent of bath creation and annihilation operators, $e^G |n\rangle \langle n| e^{-G} = |n\rangle \langle n|$ [43–45, 58].

6.3.1 Effect on super-Ohmic environments

For our analysis, let's first consider a super-Ohmic environment where $\alpha = 3$, $l = 1.1$, $\omega_c = 3$ THz, $T = 300$ K and system with site energies $\epsilon_1 = \epsilon_2 = 1.5$ THz and $\epsilon_3 = 0$. The corresponding spectral density function is given by,

$$J_2(\omega) = q\omega_c \left(\frac{\omega}{\omega_c} \right)^3 \exp \left(\frac{-1.1\omega}{\omega_c} \right) \left| \ln \left(\frac{\omega}{\omega_c} \right) \right|^n. \quad (6.26)$$

Figure 6.3 demonstrates the plots we obtained for (a) $q=0.1$ and $V_{12} = V_{23} = 0.6$ THz, (b) $q=0.5$ and $V_{12} = V_{23} = 6$ THz, (c) $q=0.2$ and $V_{12} = V_{23} = 9$ THz while altering the logarithmic perturbation factor n . By observing the donor population in Figure 6.3(a) where variational quantum master equation operates in the intermediate coupling regime, when system and bath parameters are comparable to each other, it can be noticed that $n=0$ graph shows the most coherent energy transfer dynamics out of all four graphs. Besides, as the value of logarithmic factor (n) decreases we see coherent oscillations have vanished in a truncated time period. On the other hand, larger n value indicates that the donor population takes a longer time to attain the steady state. These behaviours are consistent for both acceptor populations A_1 and A_2 .

In Figure 6.3(b), we illustrate the effect from logarithmic perturbations in a system near the Förster limit in a multisite system where $q=0.5$ and $V_{12} = V_{23} = 6$ THz. It is interesting to mention that relaxation dynamics occur in a brief time frame than the previous case, with relatively a low quantum coherence effect. As in the case for Figure 6.3(a), we observe a reduction in the long term coherent dynamics when we decrement the value of logarithmic perturbation factor n . Moreover, steady state site populations indicates that when $n = -0.65$, an efficient transfer has taken place by comparing to other three logarithmic perturbation factor values. With respect to the short term coherent dynamics, $n = 0$ and $n = -0.25$ graphs closely follow each other in all three site populations. Despite the fact that both $n = -0.5$ and $n = -0.65$ graphs in donor population and acceptor 1 population illustrates coherent oscillatory dynamics, corresponding graphs in acceptor 2 population demonstrates purely an incoherent transfer. This indicates that energy is transferred from site to site, it is possible to lose quantum coherence if the environment is perturbed with a higher negative perturbation factor.

Furthermore, Figure 6.3(c) demonstrate coherent energy transfer dynamics near Redfield limit where $q=0.2$ and $V_{12} = V_{23} = 9$ THz. Evidently, we observe that when we reduce the logarithmic perturbation factor, quantum coherence effects have been decreased where $n = -0.65$ graph indicates the largest decay out of all graphs.

Therefore, it is evident that these logarithmic perturbations affect the coherent energy transfer appears in all three coupling regimes. In the intermediate coupling regime and the Förster limit, we observe that coherent oscillations are only sustained over a brief time when perturbed by a larger negative logarithmic factor. Further, in these two coupling regimes, the effect from higher negative factors is more apparent than the Redfield limit where environmental influence is inferior compared to the former coupling regimes.

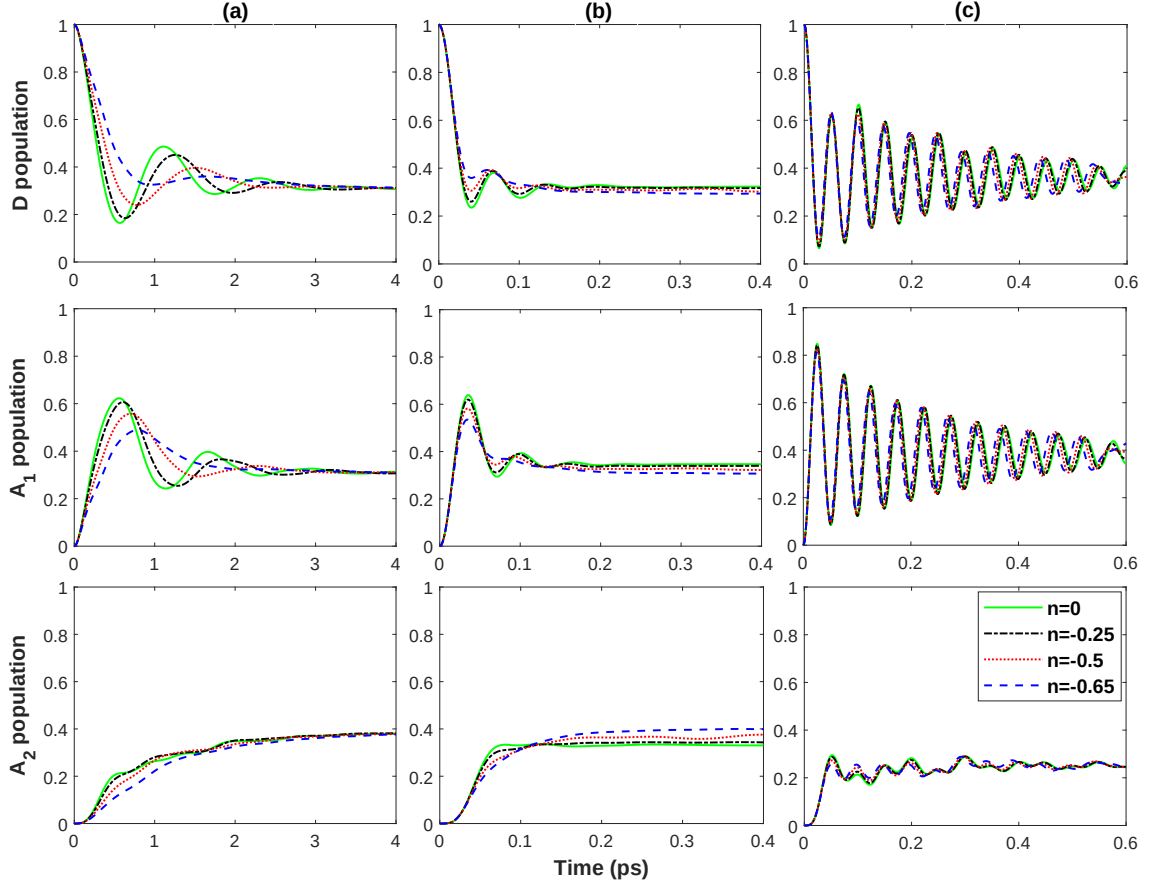


Figure 6.3: Population at D , A_1 and A_2 for $J_2(\omega)$ super-Ohmic environment SDF with (a) $q=0.1$ and $V_{12} = V_{23} = 0.6$ THz (b) $q=0.5$ and $V_{12} = V_{23} = 6$ THz , (c) $q=0.2$ and $V_{12} = V_{23} = 9$ THz. For all cases $\alpha = 3$, $l = 1.1$, $\omega_c = 3$ THz, $\epsilon_{12} = \epsilon_{23} = 1.5$ THz and $T = 300$ K has been considered.

6.3.2 Effect on Ohmic environments

Next, let's consider an Ohmic environment where $l = 1.1$, $\omega_c = 3$ THz, $q = 0.01$, $T = 300$ K and system site energies $\epsilon_1 = \epsilon_2 = 1.5$ THz and $\epsilon_3 = 0$. The corresponding spectral density function is given by,

$$J_3(\omega) = 0.01\omega_c \left(\frac{\omega}{\omega_c} \right) \exp \left(\frac{-1.1\omega}{\omega_c} \right) \left| \ln \left(\frac{\omega}{\omega_c} \right) \right|^n. \quad (6.27)$$

Figure 6.4(a) illustrates a system near to the Förster limit where we observe a reduction in the oscillations when logarithmic perturbation factor is decreased from

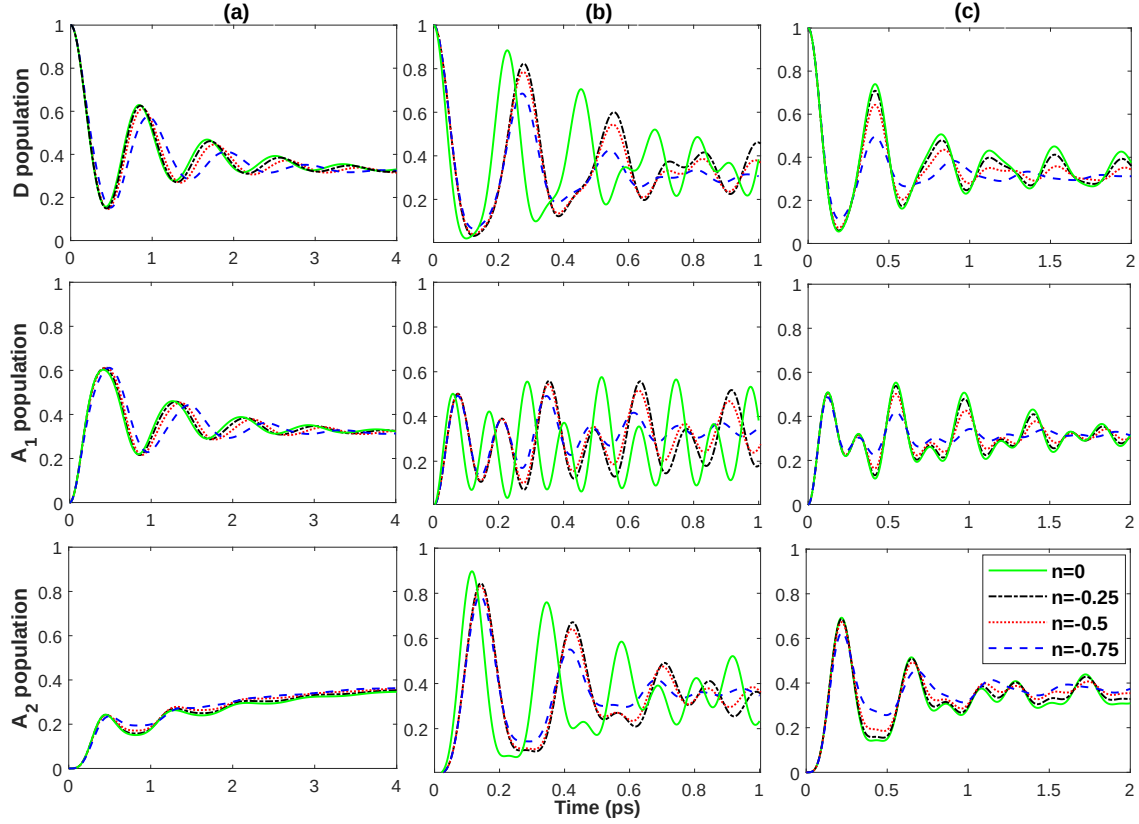


Figure 6.4: Population at donor for $J_3(\omega)$ Ohmic environment SDF with (a) $V = 0.6$ THz (b) $V = 2.4$ THz and (c) $V = 1.5$ THz. For all cases $\alpha = 1$, $l = 1.1$, $\omega_c = 3$ THz, $\epsilon_1 = \epsilon_2 = 1.5$ THz, $\epsilon_3 = 0$, $q = 0.01$ and $T = 300$ K has been considered.

$n=0$ to $n=-0.75$. In fact, when n is reduced frequency of the coherent oscillations have increased over time.

Futhermore, a system near to the Redfield limit indicates that variations in the logarithmic factor critically govern the overall dynamics as shown in Figure 6.4(b) despite the fact that in the Redfield limit system-site coupling strength is minimal. As in the previous case, amount of observed quantum coherent dynamics have been noticeably reduced in the strong site-site coupling regime, especially when $n=-0.75$. We can corroborate that some oscillations have entirely diminished when comparing $n=0$ and $n=-0.75$ graphs. Moreover, we clearly observe that oscillations are shifted to the right as we decrease the logarithmic factor. In Figure 6.4(c), when the system operates in the intermediate coupling regime, we

see a similar behaviour to Figure 6.4(a) where a decrease in logarithmic perturbation factor has resulted in reducing the oscillatory dynamics. The most notable characteristic of this figure is that each graph has the same oscillatory frequency except for $n=-0.75$ graph. Due to the fact that decreased logarithmic factor ($n=-0.75$) has reduced the overall system-bath coupling to a point where the quantum master equation now operates closer to the Förster limit.

Therefore, in all three coupling regimes in Ohmic environments we observe that in general, not only coherent oscillatory dynamics get reduced but also the frequency of the oscillations are decreased as we decrease the logarithmic perturbation factor.

This behaviour is clear in the Förster limit and the intermediate coupling regime whereas in the Redfield limit environmental effects such as logarithmic perturbations don't play a significant role. Important fact to note here is the behaviour of the energy transfer when logarithmic perturbation factor is negative in the intermediate coupling regime whereby an efficient transfer has been manifested.

6.3.3 Comparison with full-polaron transformation

Finally, in an effort to compare the performance of full polaron transformation based QME and the variational polaron transformation based QME, we plot Figure 6.5 using multisite full polaron transformation based QME where all parameters are equivalent to Figure 6.3. It is clearly evident that in the intermediate coupling regime, all three graphs for case (a) looks identical for both theories. This is due to the fact that both theories coincide in terms of bath correlation functions in this regime.

Figure 6.3(b) and Figure 6.5(b) illustrate a configuration near to the Förster limit and full polaron transformation based QME manifests an energy transfer

with an absence of coherent oscillatory dynamics. It can be observed that in the short term dynamics, an increment of the perturbation factor can slightly alter the time it takes to reach the steady state population. Variational polaron transformation based QME not only reveals coherent dynamics but also indicates distinguishable effects from logarithmic perturbations in the quantum environment. In

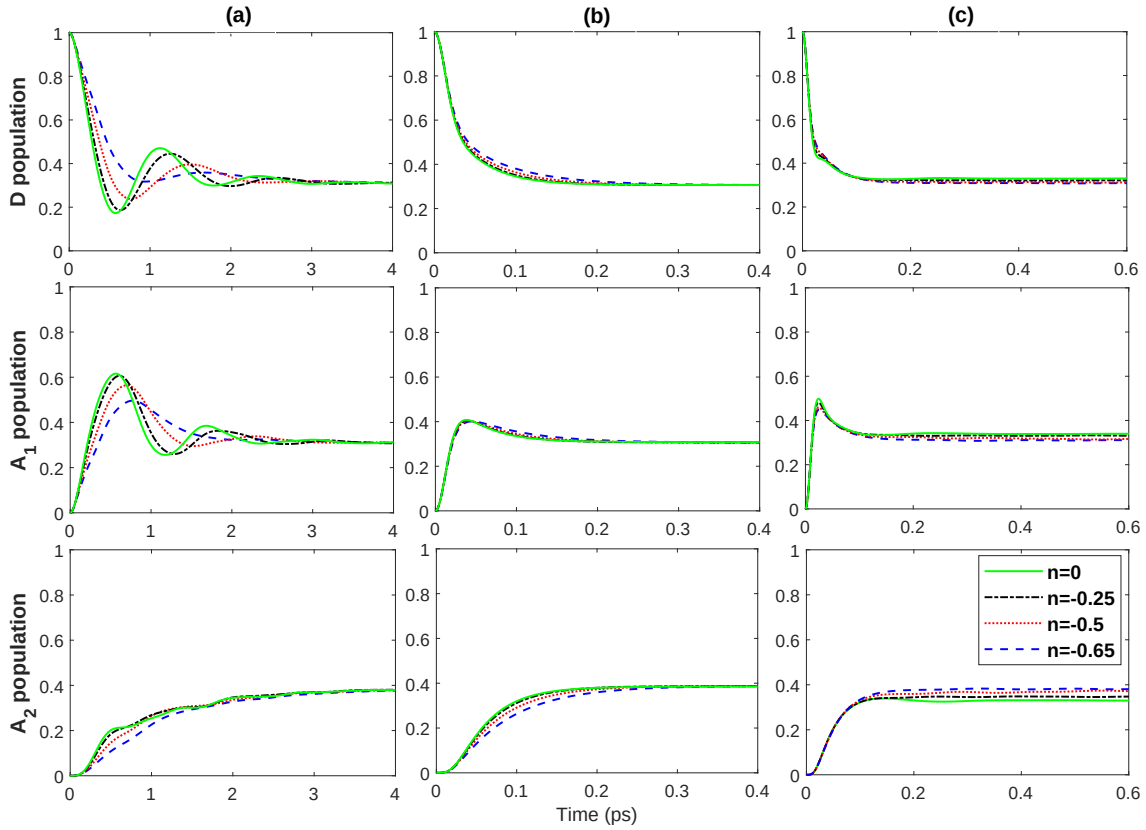


Figure 6.5: Population at D , A_1 and A_2 for $J_4(\omega)$ super-Ohmic environment SDF with (a) $q=0.1$ and $V_{12} = V_{23} = 0.6$ THz (b) $q=0.5$ and $V_{12} = V_{23} = 6$ THz, (c) $q=0.2$ and $V_{12} = V_{23} = 9$ THz. For all cases $\alpha = 3$, $l = 1.1$, $\omega_c = 3$ THz, $\epsilon_{12} = \epsilon_{23} = 1.5$ THz and $T = 300$ K has been considered.

the Redfield limit, we observe vastly contrasting results when comparing Figure 6.3(c) and Figure 6.5(c). While variational polaron transformation based QME indicates high frequency oscillations, full polaron transformation based QME simulates an incoherent energy transfer. This is owing to the fact the bath correlation function $\phi_n^{xy}(t)$ utilizes in full polaron theory diminishes in the variational

polaron theory in the Redfield limit where it uses only $\phi_n^{zz}(t)$ bath correlation function. The counter behaviour corroborates when examining $\phi_n^{xy}(t)$ and $\phi_n^{zz}(t)$ functions where $\phi_n^{xy}(t)$ uses the term $F_n(\omega)$ and $\phi_n^{zz}(t)$ uses $1 - F_n(\omega)$ term.

Therefore, when comparing both polaron based theories, it is evident that variational polaron transformation based QME performs substantially well in capturing quantum coherent dynamics of systems in quantum environments, experiencing logarithmic perturbations in all three coupling regimes when compared to full polaron transformation based QME. While both theories perform identically in the intermediate coupling regime, the performance of full polaron theory in both Förster limit and Redfield limit is disappointing in terms of simulating coherent energy transfer dynamics. Another limitation of full polaron theory is that in Ohmic environments, it suffers from well known infrared divergence effect. Thus, it can only be utilized in super-Ohmic environments.

6.4 Summary and Conclusions

In summary, we have outlined the coherent energy transfer among three interacting chromophores attached to quantum environments with logarithmic perturbations utilizing a multichromophoric variational polaron transformation based quantum master equation. We have specifically analysed the energy transfer when the quantum system suffers from negative logarithmic perturbation factor, in Förster limit, Redfield limit, and the intermediate coupling regime for both Ohmic and super-Ohmic environments. In what follows, we have compared the performance of full polaron theory and variational theory in this multichromophoric system to comprehend the most suitable theory to delineate energy transport of aforementioned quantum systems.

We discovered that negative logarithmic perturbations could alter the coherent dynamics in all three system-bath coupling regimes in super-Ohmic environ-

ments. Larger negative perturbation values can reduce the oscillatory dynamics and force the energy transport to the incoherent regime. Furthermore, an efficient transfer has been manifested for more prominent negative perturbation factors near the Förster limit. The pattern of larger negative perturbation values diminishing the coherent oscillatory dynamics was not confined to super-Ohmic environments, in fact, Ohmic environment manifested the same behaviour. It is also important to note that the time scale of the energy transfer has shifted right when these logarithmic perturbations are present in the environment.

When comparing the full polaron theory and the variational theory, it was evident that variational theory is capable of simulating underlying quantum coherence in the multichromophoric system in all three coupling regimes and is superior to full polaron theory when simulating energy transport when systems are linked to environments with logarithmic perturbations. In both Förster limit and Redfield limit, full polaron theory manifested an incoherent energy transfer due to incapacities of grasping coherent behaviour from the existing bath correlation function owing to its full polaron approximation.

In conclusion, the results obtained in this study are vital in apprehending energy transport in quantum environments that are slightly different from its original form. We have delineated that it is possible to reduce the quantum coherence of an energy transfer of a given system by introducing logarithmic perturbations of negative values to attached quantum environments. Besides, we have manifested the fact that there is a possibility of shifting the energy transport into the incoherent regime by incrementing the negative logarithmic factor value, which can be used in future studies given the requirement.

Chapter 7

Contributions and Future work

7.1 Summary of Contributions

This section outlines our research objectives, how the related research was carried out and a summary of the outcomes of that research objective.

Research objective 1 - Analytical characterization of coherent resonance energy transfer dynamics of a two level system coupled to ohmic-like environments with full polaron transformation approach

Under our first research objective, we have analysed a two-level interacting donor-acceptor pair in a disturbed quantum environment. Utilizing the combined system Hamiltonians and the Liouville's super operators, we proceeded to come up with a quantum master equation based on second-order perturbation theory. In order to, allow this quantum master equation to be applicable for both weak and strong bath coupling regimes, we have employed full polaron transformation. Since this particular type of polaron transformation is only applicable for super-ohmic environments without suffering infrared divergence effect, we have analysed the coherent energy transfer dynamics of the interacting donor-acceptor pair in such an environment. Furthermore, to divert the spectral density function of the quantum environment from the standard ohmic function, we have incorporated positive powers of logarithmic factors which are innate in low frequency

power series expansion of the spectral density.

Our results demonstrate that for larger system bath coupling strengths, full polaron based quantum master equation is unable to provide accurate results whereas for weaker system bath coupling strengths, it performs better. Further, for a given system bath coupling strength, as logarithmic perturbations are increasing, the damping characteristics of the coherent energy transfer are also increasing. In addition, we show that smaller values of the Ohmicity parameter can suffer severe distortions even for a small logarithmic perturbation. Doing so, we show that full polaron transformation-based quantum master equation is capable of undergoing infrared divergence even for a super Ohmic environment, when higher orders logarithmic perturbations are present.

Research objective 2 - Investigating coherent resonance energy transfer using a quantum master equation in variational polaron frame

For the second research objective, we have exploited an interacting pair of chromophores attached to a quantum environment which is different from standard sub ohmic, ohmic and super ohmic categorization of the spectral density functions. We have considered that chromophores have two energy levels and initially all the energy is at the donor chromophore which we have pumped through a laser pulse. Concomitant energy transfer has been studied utilizing a quantum master equation derived using the variational polaron transformation function. Coherent energy transfer dynamics were simulated by altering the ohmicity parameter, system-bath coupling strengths and the value of positive logarithmic factor in the environment.

Our results demonstrate that even for a relatively large bath coupling strength, quantum coherence effects can be increased by introducing logarithmic perturbations of the order of one and two in super-Ohmic environments. Moreover, for particular values of the Ohmicity parameter, the effect of logarithmic perturba-

tions is observed to be insignificant for the overall dynamics. In regard to Ohmic environments, as logarithmic perturbations increase, damping characteristics of the coherent transient dynamics also increase in general. It is also shown that, having logarithmic perturbations of the order of one in an Ohmic environment can result in a less efficient energy transfer for relatively larger system bath coupling strengths.

Research objective 3 - Analysing coherent resonance energy transfer of a multi site system under logarithmic perturbations utilizing full polaron based quantum master equation

One of the more popular approximation methods in simulating the energy transfer is the multi-site exciton full polaron transformation-based quantum master equation which has shown the ability to interpolate between weak and strong system bath coupling regimes. In our third research objective, we analysed the energy transfer among three interacting chromophores employing above quantum master equation when the quantum system in disturbed environment using positive logarithmic factors. We also analysed the applicability of this quantum master equation by gauging its performance by altering system-bath coupling strengths in addition to the magnitude of the logarithmic factor.

Our results reveal that, when system bath coupling strength is larger the derived multi-exciton full polaron transformation-based quantum master equation is unable to simulate accurate dynamics where in some scenarios the well-known phenomena of infrared divergence occur. On the other hand, when the system bath coupling strength is weak, derived equation conveys better results. In addition, results show that smaller Ohmicity values can suffer from acute distortions even for a smaller logarithmic perturbation. Also, we show that when logarithmic perturbations are increased, damping characteristics of the energy transfer are also increased in general.

Research objective 4 - Performance of variational transformation based quantum master equation in terms of simulating coherent resonance energy transfer in a multi exciton transport system under logarithmic perturbations

Our final research objective, we have considered a multi exciton system consists of a donor chromophore and two acceptor chromophores, which we analysed through multisite variational polaron transformation based quantum master equation. We once again coupled a disturbed quantum environment which now undergoes negative logarithmic perturbations to this multi chromophoric system. We then proceeded to simulate the coherent resonance energy transfer dynamics in disturbed super ohmic and ohmic environments by varying a range of system and bath specific parameters to identify the effects they enforce on the said transfer.

Our results delineate that negative logarithmic perturbations can decrement the quantum oscillatory dynamics throughout the energy transferring path. More prominent negative logarithmic factors can force the energy transfer to the incoherent regime. We further demonstrated that this behavior is consistent in all three coupling regimes in Ohmic and super-Ohmic environments. Our results indicate that an efficient transfer can occur for more prominent negative logarithmic factors near the Forster limit in super-Ohmic environments. Finally, we compare the multichromophoric variants of full polaron-based quantum master equation and the variational polaron-based quantum master equation. We find that variational theory performs seamlessly in all three coupling regimes where full-polaron theory suffers from its full-polaron approximation.

7.2 Suggestions for Future Work

This section presents feasible proposals for future explorations that can be extended based on the work presented in this thesis.

Investigating the impact on various coherent initial conditions

Contemporary literature includes studies into various coherent initial conditions such as shown in [46]. These studies discuss the initial state of the interested quantum system to be a mix state where donor and acceptor chromophores share the excited energy. In this thesis, we have assumed that initially, the donor chromophore would contain all the energy which acts as a boundary condition for our analysis. But the analysis where energy is shared between the interacting chromophores, is essential since this scenario happens more often in photosynthesis and RET based applications. Such a study would be interesting to see when the quantum systems are coupled to environments with logarithmic perturbations of positive and negative magnitudes.

Modelling the bath correlations in disturbed environments

The analysis we have presented in this thesis has assumed that donor and acceptor chromophores are attached to identical and independent baths. Such an assumption is not typically valid when these interacting chromophores are physically in the proximity of each other. When relaxing this assumption, bath correlations between the bath modes attached to donor and acceptor chromophores impact the simulating energy transfer. Such bath correlations are studied in various studies found in the literature [45,50] but it would be very insightful to look at such bath correlations when the bath is disturbed by logarithmic perturbations. It will also be interesting to explore the coherent resonance energy transfer dynamics when bath correlations are present.

Exploring the effect from the inhomogeneous term to overall dynamics

The quantum master equations based on second order perturbation theory include a homogeneous term as well as an inhomogeneous term [45]. Homoge-

neous term mainly carries the larger portion of the dynamics mostly related to system evolution and the inhomogeneous term consists of non-Markovian dynamics relate to energy dissipation and absorption. This thesis has studied disturbed quantum environments and the energy transfer dynamics in such environments utilizing only the homogeneous term in the quantum master equation assuming the contribution of inhomogeneous term is minimal. But for an accurate analysis, this term also should be considered. A future study on the contribution of inhomogeneous term in disturbed environments would be interesting.

Investigating initial bath correlations' impact on the energy transfer

Another assumption that we have made in this work is the fact that, at $t=0$, system density matrix and the environmental density matrix could be separated. Such an assumption is vital in deriving the quantum master equation using the second-order perturbation theory. By relaxing this restriction, one can assess the energy transfer dynamics of deviated quantum environments with exceptional accuracy. This process may entail complex mathematical derivations with reasonable assumptions, but such work would be important in full realization of energy transfer in this area.

Comparison with presented results vs FRET theory

In this thesis, we have investigated logarithmic perturbations of positive and negative magnitudes and their impact on overall coherent resonance energy transfer dynamics. Analyses performed were using variational and full polaron transformation based quantum master equations. Another quantum master equation which can simulate energy transfer dynamics, is FRET theory [1] which is equivalent to when there is no polaron transformation applied. Even though, FRET theory cannot capture coherent dynamics, such study could explore how devi-

ated quantum environments can impact FRET rate of quantum, semi-classical and classical systems.

Modelling logarithmic perturbations to induce them into the bath modes experimentally

Logarithmic perturbation factors used in this study are utilized to deviate the spectral density function of quantum environments from the common categorization of sub-ohmic, ohmic and super-ohmic environments. It has been shown that, low frequency power series expansions of spectral density functions consist of logarithmic terms of various orders [51]. Means of inducing these logarithmic perturbations externally would be a step towards future realization of applications which could use our theoretical framework. Such experiments can also pave the way to explore how these perturbations can be enhanced, reduced and controlled in potential applications.

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