

# **Open Quantum System: Dynamics and equilibrium state in weak and ultrastrong coupling limits**

*By*

**Prem Kumar**

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 Date: 08.09.2026

Chair - Sanatan Digal

 Date: 08.09.2026

Guide/Convener - Sibasish Ghosh

 Date: 08.09.2026

Member 1 - Ajit C. Balram

 Date: 08.09.2026

Member 2 - Pinaki Chaudhuri

 Date: 08.09.2026

Member 3 - Arul Lakshminarayan

 Date: 08.09.2026

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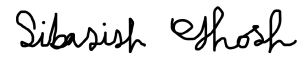


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Sibasish Ghosh

Professor

Theoretical Physics

IMSc, Chennai



## List of Publications arising from the thesis

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1. **“Ultrastrong coupling limit to quantum mean force Gibbs state for anharmonic environment”**

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*To my mother and father,  
and my brother and sisters,  
and my nephew and nieces.*

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# Abstract

The spin-boson model is a widely used model for understanding the properties of a two-level open quantum system. Accurately describing its dynamics often requires going beyond the weak system-environment coupling approximation. This work presents the analytical derivation of the complete fourth-order time-convolutionless (TCL) generator for a generic spin-boson model, accurate up to 4th order in the system-environment coupling parameter, for a very general class of environmental spectral densities. We use a higher-order quantum master equation (in system environment coupling strength) to analytically calculate all the deviations of the steady state of the quantum system up to second order in the coupling strength. We also show that this steady state is exactly identical to the corresponding generalized Gibbs state, the so-called quantum mean force Gibbs state, at arbitrary temperature. In the case of a semiconductor double-quantum-dot system, our results reveal corrections to the dynamics that may become physically significant in some parameter regimes. Furthermore, we report that the widely used second-order TCL master equation tends to overestimate the non-Markovianity of a dynamics over a large parameter regime. The accuracy of the fourth-order TCL generator is rigorously benchmarked against specialized analytical calculations done for the Ohmic spectral density with Drude cutoff and against the numerically exact Hierarchical Equations of Motion technique.

The equilibrium state of a quantum system can deviate from the Gibbs state if the system-environment (SE) coupling is not weak. An analytical expression for this mean force Gibbs state (MFGS) is known in the ultrastrong coupling (USC) regime for the Caldeira-

Leggett (CL) model that assumes a harmonic environment. Here, we derive analytical expressions for the MFGS in the USC regime for more general SE models. For all the generalized models considered here, we find the USC state to be diagonal in the basis set by the SE interaction, just like in the CL case. While for the generic model considered, the corresponding USC-MFGS is found to alter from the CL-result, we do identify a class of models more general than the CL model for which the CL-USC result remains unchanged. We also provide numerical verification for our results. These results provide key tools for the study of strong coupling quantum thermodynamics and several quantum chemistry and biology problems under more realistic SE models, going beyond the CL model.

# Notation and Conventions

- Throughout this thesis, we assume that  $\hbar = k_B = 1$ . We also assume implicit units for energy and length, denoted by  $E_0$  and  $L_0$ , respectively, all set to unity. For concreteness, since we apply our results to a double quantum dot system, we set  $L_0 = 150$  nm and  $E_0 = 2.1 \times 10^{-24} J$  in terms of SI unit [1].

All other units are expressed in terms of these reference units. For example, it will be convenient to define the unit of mass as  $M_0 = 1/(E_0 L_0^2) \approx 2.4 \times 10^{-31} \text{kg}$ .

- $J(\omega)$  refers to the spectral density of the environment and  $f(\omega)$  is a shorthand for  $J(\omega) \coth(\beta\omega/2)$ , where  $\beta$  is the inverse temperature of the environment.

## Acronyms:

- TCL: Time-Convolutionless
- ME: Master Equation
- TCL2n: TCL-ME up to order  $2n$  in system-environment coupling strength.
- SBM: Spin-Boson Model
- SS: Steady State
- MFGS: Mean Force Gibbs State
- SE: System-Environment

- BR: Bloch-Redfield
- DQD: Double Quantum Dot
- BLP: Breuer-Laine-Piilo
- HEOM: Hierarchical Equations of Motion
- CPTP: Completely Positive Trace Preserving
- CP: Completely Positive
- GKSL: Gorini-Kossakowski-Sudarshan-Lindblad
- USC: Ultra-Strong Coupling
- CL: Caldeira-Leggett
- GCL: Generalized Caldeira-Leggett
- GCL2: Generalized Caldeira-Leggett (Subclass)
- CV: Continuous Variable
- PE: Potential Energy
- TP: Trace Preserving

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# Chapter 1

## Introduction

### 1.1 Motivation

Many realistic quantum systems interact with their surrounding environment, leading to phenomena like dissipation and decoherence, which provide modifications to the Schrodinger equation. This necessitates the framework of open quantum systems, where we study the dynamics of a system of interest by tracing out (averaging over) the degrees of freedom of its environment. The full system–environment (SE) dynamics is still governed by the Schrodinger equation. However, because we are often not interested in (and frequently cannot feasibly track) the environmental degrees of freedom, we instead study the effective dynamics at the level of the system alone.

The Bloch-Redfield (BR) master equation (ME) provides environmental corrections to the dynamics of an open quantum system in the weak SE coupling limit. BR-ME is a cornerstone in the theory of open quantum systems and is widely adopted in diverse fields such as quantum chemistry and biology, thermodynamics, quantum information, computing, and technology to model the effect of an environment on a quantum system [2–4]. Its usefulness, however, comes with an important limitation: it retains only the leading contribution of the coupling. As quantum technologies increasingly rely on precise control

of small systems such as individual qubits, the corrections omitted at leading order can affect theoretical predictions. A systematic description beyond the BR-ME is therefore needed both for accurate modelling and for understanding where the standard approximation ceases to be sufficient.

The same limitation leads directly to a fundamental question about equilibration. It is textbook knowledge that many systems, when in contact with a large environment at some temperature, equilibrate to the standard Gibbs state in the long-time limit. But when the system-environment coupling is not negligible, the corresponding equilibrium state is known to deviate from the Gibbs state. This modified equilibrium state is called the mean force Gibbs state (MFGS) [5]. Although for a macroscopic system, the resulting correction may be insignificant, that need not be the case for a small quantum system, such as a single qubit. These corrections to the Gibbs state are hence of fundamental interest in the field of strong-coupling quantum thermodynamics. The correspondence between the dynamical steady state and this MFGS is hence a central open problem in the field. Thus, the need to go beyond the BR-ME and the question of equilibration beyond the Gibbs state are two aspects of the same problem. This thesis makes some contributions to different aspects of these two directions.

The first central result of this thesis concerns the dynamics in the weak-coupling regime beyond leading order. For the spin-Boson model (SBM), which describes a qubit coupled to a bosonic environment, the thesis derives and simplifies the next-order time-convolutionless (TCL) ME for a very general class of model parameters. The SBM has many applications, one of them being in quantum technology [6, 7]. Our result makes the higher-order dynamics and steady state analytically calculable, allowing us to prove the approach to the MFGS beyond the leading order. We also apply the next-order ME we derive to the dynamics of a semiconductor double-quantum-dot (DQD) system. We use our results to examine how the higher-order correction changes non-Markovianity, quantified using the Breuer-Laine-Piilo (BLP) measure. One key finding here is that the

BR-ME tends to over-estimate the non-Markovianity over a large model parameter regime considered by us, indicating that a higher coupling regime can also suppress the memory effects rather than enhancing them. Our results are benchmarked against the hierarchical equations of motion (HEOM), an established nonperturbative, numerically exact method. The derivation of the higher-order ME exposes an interesting though technical integration-order subtlety, where the chosen order of a double frequency integral is required to be obeyed consistently for all the terms involved to avoid discrepancies in the final result.

The second direction concerns equilibration at ultrastrong coupling (USC), the opposite limit from the usual weak-coupling expansion. Existing analytical MFGS results generally model the environment as harmonic, although anharmonic effects are important in several chemical and condensed-phase settings. Using the Feynman-Vernon influence-functional approach, the thesis analytically extends USC-MFGS results to specified classes of anharmonic environments. It identifies which structural features of the harmonic result survive, and tests the analytical predictions by direct numerical calculations on small examples.

Together, these two parts connect dynamics and equilibrium from complementary coupling limits. We will now discuss some technical details of the results obtained in this thesis.

## 1.2 Technical setting

It is known that the textbook Gibbs state is the steady state (SS) of a quantum system only in the vanishing SE coupling limit. The BR-ME correctly predicts the  $O(\lambda^2)$  deviation of the coherence of a quantum state from the Gibbs state [8–10], where  $\lambda$  is the SE coupling parameter. However, the populations predicted by BR-ME are correct only up to  $O(1)$ . In fact, it is a general fact that a perturbative ME up to  $O(\lambda^{2n})$  is able to predict the coherence

of SS and populations up to  $O(\lambda^{2n})$  and  $O(\lambda^{2n-2})$ , respectively [9]. Since the BR-ME is a  $O(\lambda^2)$  ME, to obtain a more accurate dynamics of an open quantum system and to capture any deviation of the SS populations from the Gibbs state, we need to go to a higher order ME.

The time-convolutionless (TCL) projection operator method is a scheme to perturbatively derive a ME of the order of even powers of the SE coupling parameter  $\lambda$  [3]. An  $O(\lambda^{2n})$  TCL-ME is usually denoted as TCL2n-ME. In fact, BR-ME is equivalent to TCL2. We hence need to solve TCL4 in order to correctly predict the SS populations up to  $O(\lambda^2)$ . But higher order TCL generators are quite difficult to calculate. It may be noted here that some progress has been made in efficiently evaluating these higher order MEs (see, e.g., [8, 11–13]). Before getting into further details about the SS of a quantum state, we discuss a related concept called the mean force Gibbs state (MFGS), which is a natural generalization of Gibbs state of a quantum system when the SE coupling strength is non-negligible [5].

The MFGS is formally defined as

$$\hat{\rho}_{MF} = \text{Tr}_E Z^{-1} e^{-\beta \hat{H}_{SE}}, \quad (1.1)$$

where  $\hat{H}_{SE}$  is the full SE Hamiltonian,  $Z = \text{Tr} e^{-\beta \hat{H}_{SE}}$  and  $\beta$  is the inverse temperature of the environment. We can see that the MFGS reduces to the textbook Gibbs state,  $\hat{\rho}_G = Z_S^{-1} e^{-\beta \hat{H}_S}$ , in the vanishing SE coupling limit, where  $Z_S = \text{Tr}_S e^{-\beta \hat{H}_S}$  and  $\hat{H}_S$  is the system Hamiltonian [5]. Hence, MFGS can be seen as the appropriate equilibrium state of a quantum system when the SE coupling is non-negligible.

The MFGS has many applications, for example in the field of strong-coupling quantum thermodynamics [14–17, 17–21]. Second order perturbative expression (in SE coupling strength) for the MFGS in weak coupling is known analytically for the Caldeira-Leggett (CL) model [22]. The CL model consists of a quantum system bilinearly coupled to an

environment modelled as a set of uncoupled quantum harmonic oscillators [3,4]. Under the CL-model, if the system itself is a harmonic oscillator, the MFGS can be calculated exactly for arbitrary coupling strength and temperature and can also be shown to be the SS of the corresponding exact ME [5].

It has been proven that there always exists a finite and small value of  $\lambda$  for which the SS and MFGS correspond to each other, although the proof of whether this is true for arbitrary values of  $\lambda$  is unavailable [5, 23–31]. In addition, this upper bound on  $\lambda$  is known to decrease with decreasing temperature. In fact, at zero temperature, a violation of the equivalence between SS and MFGS has also recently been reported [11]. This makes the proof of the correspondence between the SS and the MFGS up to  $O(\lambda^{2n})$  at arbitrary temperatures of high interest.

Under the assumption that, in the expression for the SS, the value of the coherences can be analytically continued to the populations, Thingna et al. have proven that second order SS matches with the corresponding expression for the MFGS, without requiring the calculation of complicated higher order generators for time evolution [9]. Using a more direct technique, DiVincenzo et al. [8] have proven this result for an SBM with Ohmic spectral density and exponential cutoff in the large cutoff limit. Recently, TCL4-ME has been used to numerically show this result at zero temperature for ohmic spectral density with exponential cutoff. [11]. In addition, cumulant ME has recently been used to give a better approximation to the second order SS than BR and other equations [32,33].

The SBM consists of a two level quantum system coupled to many Bosonic modes, uncoupled from each other [3,4] (see Fig. 1.1).

The SBM is a powerful model that has found wide scale applications in diverse fields from quantum chemistry and biology to many body physics and quantum information, computing, and technology. For example, the SBM has been used to study bio-molecule systems like chromophores and photosynthetic complexes [34–36], trapped ions [7], electron transfer reactions [37,38] and superconducting circuits [6].

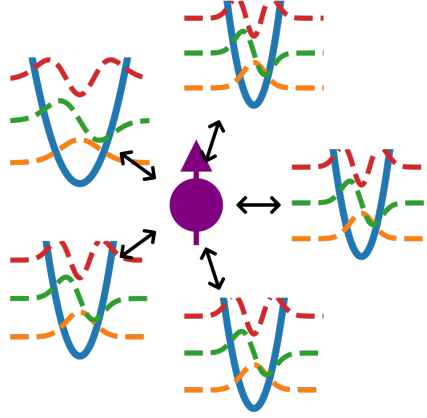


Figure 1.1: Pictorial representation of the Spin-Boson model (SBM), one of the central models of open quantum systems studied in this thesis. The SBM consists of a two-level quantum system, like a spin-1/2 system, interacting individually with a large number of non-interacting bosonic modes, like phonons. Each environmental mode is initially assumed to be in a thermal state at a common temperature  $T$ .

The results in this thesis can be divided into two main parts: the analytical derivation and applications of TCL4-ME for SBM in the weak coupling limit, and the generalization of the strong coupling MFGS from harmonic to a large class of anharmonic environments. We will now discuss both these results one by one.

### 1.3 Higher order master equation for Spin-Boson model

One of our main results is the derivation of the full asymptotic TCL4 generator for the generic SBM, for a broad class of spectral density [39]. We have been able to reduce the final expression for the coefficients of the TCL4 generator to, at most, a double integral over frequency variables, which, without knowing the specific form of the spectral density, cannot be further simplified. This has greatly facilitated both symbolic analysis and numerical evaluation of the TCL4 dynamics and SS. For example, our results have enabled us to analytically evaluate the 4th-order corrections to the SS coherences of the system.

Next, for a generic SBM at arbitrary temperature, we analytically prove the equivalence

between SS and MFGS up to  $O(\lambda^2)$  in coupling using TCL4 generator [40]. We do this in a very general setting, for a broad class of environmental spectral density. In particular, we apply our results to study the dynamics and the steady state of a semiconductor double-quantum-dot (DQD) embedded on a substrate [1, 41–47] which models a charge qubit coupled to a phononic bath [48, 49].

We also study the corrections to non-Markovianity induced by TCL4 in the dynamics of TCL2-ME, quantified by the BLP measure [50]. We report that for the majority of the parameter regime considered, TCL2 tends to overestimate the non-Markovianity of a dynamics. Recently, Alhäuser and Breuer performed a complementary analysis for the Fano-Anderson model, comparing the second- and fourth-order TCL expansions with the exact dynamics and examining their transient and steady-state behavior and their ability to capture non-Markovianity [51].

The accuracy of the TCL4 generator is rigorously benchmarked against specialized analytical calculations done for the Ohmic spectral density with Drude cutoff and against the HEOM. Finally, all the results mentioned in this work, including symbolic derivations, final expressions, numerical evaluation for specific parameters, and plots, etc, in their complete form, have been made publicly available as the accompanying supplementary material [52].

Since SBM has wide scale applications, this makes our results of widespread interest. Our results are also an important step in the direction of exactly calculating the generators for higher order MEs in a general setting, to move to the non-Markovian regime that serves as a better model for many systems of physical interest, in general. Moreover, our results also serve as a validation of the analytic continuation assumption used by Thingna et al. [9] for SBM.

## 1.4 Ultra-Strong Coupling Mean Force Gibbs State for anharmonic environment

Many of these approaches to calculate the quantum MFGS assume the CL model for the system and the environment, which assumes the harmonic environment approximation. The harmonic environment approximation has been widely successful in capturing the behavior of a variety of physical systems. [2, 4, 34, 53–67] Yet, advancement in experimental techniques and more detailed theoretical considerations have shown the inadequacy of the harmonic environment approximation, sparking numerous studies on open quantum system with anharmonic environment. [68–80] For example, for electron transfer happening in the presence of strongly coupled low-frequency intramolecular modes or an environment consisting of nonpolar liquids, the harmonic approximation is known to fail. [68–71, 75–78] It is hence worth investigating the MFGS result for SE models beyond the CL model.

For the CL model, analytical expression for the MFGS in ultrastrong coupling (USC) regime has been determined for continuous variable (CV) systems [81, 82] and, more recently, for a more general CL model (consisting of an arbitrary system Hamiltonian and coupling-operator) [22]. Moreover, this state is also confirmed to be the steady state of an ultrastrong coupling ME for harmonic environments [5].

The USC-MFGS acts as a good indicator for the deviation of the MFGS from the textbook Gibbs state at large coupling. However, since this result is only valid for the CL model, its applicability is significantly limited. It also remains uncertain as to which aspects of the USC result are artifacts of the specific structures of the CL model, and which aspects might persist when the model is generalized. Here, we attempt to address this issue by studying the USC-MFGS for models beyond the CL model (see Fig. 1.2).

We find that for all the SE models considered by us, one of the core features of the CL-

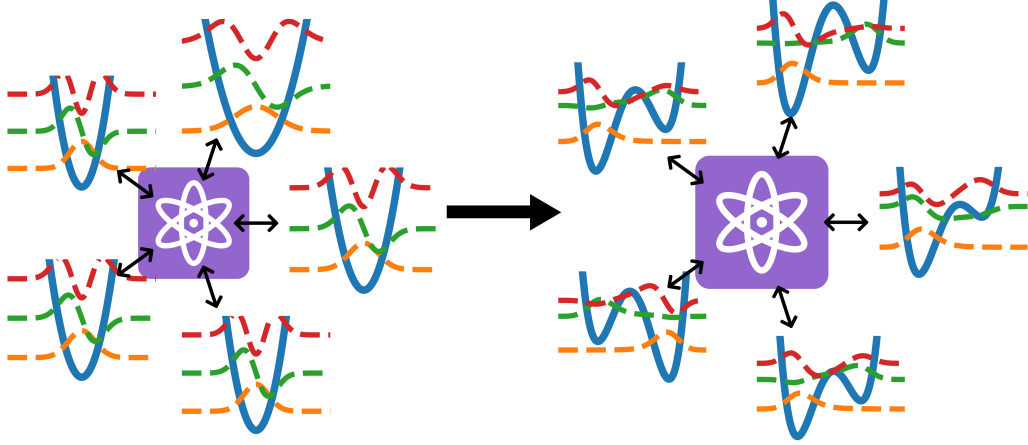


Figure 1.2: Pictorial representation of one of the central results of this thesis. The result consists of a generalization of the analytical evaluation of the ultrastrong coupling equilibrium state (MFGS) of a quantum system with harmonic environment model (left image) to a large class of anharmonic environment models (right image). The harmonic environment assumption, although widely applicable, is known to break down for some systems of physical interest.

USC result, that the MFGS is diagonal in the basis set by the SE interaction, remains intact, although the functional form of the MFGS does get affected. For example, the most general extension of the CL model considered by us, which we call the generalized Caldeira-Leggett (GCL) model, shows such deviations from the CL-USC result. Within the GCL model, we identify a subclass of models, which we call the GCL2 model, for which the CL-USC result remains exactly valid. Finally, we derive an analytical expression for the USC-MFGS for another class of model (distinct from the GCL model), the so-called Zwanzig model [83–86], and find that the corresponding USC state, although still diagonal in the basis set by the SE interaction, has qualitative distinctions from the GCL2-USC result.

## 1.5 Organization of the thesis

Both of these results, described in Secs. 1.3 and 1.4, hence encompass a wide range of physical systems and phenomena, going beyond the typical weak coupling assumption for the open quantum systems.

This thesis is structured as following:

1. **Ch 1.** is an introduction to the thesis.
2. **Ch 2.** reviews the theoretical background: We first provide a pedagogical introduction to TCL-formalism. We then introduce the SBM. This is followed by a discussion on non-Markovianity in open quantum systems. Finally, we discuss the path integral approach to determining the MFGS.
3. **Ch 3.** provides analytical derivation of TCL4 for generic SBM: We discuss the derivation of the second order SS coherences and population for the SBM, which requires the TCL2 and TCL4 generators respectively. We show the equivalence between the second order SS and MFGS for a generic SBM at arbitrary non-zero temperature. This also enables us to determine the 4th order SS coherences [40].
4. **Ch 4.** deals with the applications of the TCL4: we solve for the corrections to the dynamics and non-Markovianity of an open quantum system. We also benchmark the accuracy of the TCL4 generator against specialized analytical calculations and against the hierarchical equations of motion (HEOM) [39].
5. **Ch 5.** develops the USC-MFGS for anharmonic environments: We first review the known USC-MFGS result for the CL model. We then generalize this result to a large class of anharmonic environments. We provide numerical support for our analytical findings [87].
6. **Ch 6.** provides a summary of the results and future directions.

# Chapter 2

## Background

### 2.1 The Time-Convolutionless Master Equation

#### 2.1.1 Derivation

For completeness, here we provide a brief introduction to the theory of open quantum systems and the TCL formalism, closely following Breuer and Petruccione [3], providing the missing steps skipped in the textbook for pedagogical clarity. The TCL formalism is a systematic approach to perturbatively add corrections to the dynamics of the system in the SE coupling parameter in the weak coupling regime.

Let the total Hamiltonian of a quantum system interacting with an environment be given as:

$$\hat{H}_{SE} = \hat{H}_S + \hat{H}_E + \lambda \hat{H}_I \quad (2.1)$$

Here,  $\lambda$  denotes a dimensionless coupling parameter. Then, the evolution of the full

Hamiltonian will be given as

$$\dot{\hat{\rho}}_{SE}^{(S)}(t) = -i[\hat{H}_{SE}, \hat{\rho}_{SE}^{(S)}(t)]. \quad (2.2)$$

Here, the superscript ( $S$ ) denotes that we are working in the Schrödinger picture. We define  $\hat{H}_0 \equiv \hat{H}_S + \hat{H}_E$ . For simplicity, we assume that  $\hat{H}_0$  is time-independent. Then, for convenience, we go in the interaction picture with respect to  $\hat{H}_0$ . This means that we redefine all our operators as

$$\hat{X}^{(I)}(t) \equiv e^{i\hat{H}_0 t} \hat{X}^{(S)}(t) e^{-i\hat{H}_0 t} \quad (2.3)$$

Here, the superscript ( $I$ ) denotes the interaction picture. Then we have,

$$\frac{\partial}{\partial t} \hat{\rho}_{SE}^{(I)}(t) = -i\lambda[\hat{H}_I^{(I)}(t), \hat{\rho}_{SE}^{(I)}(t)] \quad (2.4)$$

which gives us the von Neumann equation in the interaction picture.

For brevity, we will drop the superscript ( $I$ ) from now. Next, let us define the super-operator:

$$\mathcal{L}(t)[\cdot] \equiv -i[\hat{H}_I(t), \cdot] \quad (2.5)$$

**Projecting into the relevant subspace of the full system-environment state:** Let us now define two projection operators,  $\mathcal{P}$  and  $\mathcal{Q}$ , respectively. The action of this operator on the full SE state is given as

$$\mathcal{P}\hat{\rho}_{SE} \equiv \text{Tr}_E\{\hat{\rho}_{SE}\} \otimes \hat{\rho}_E \quad (2.6)$$

$$\mathcal{Q}\hat{\rho}_{SE} \equiv \hat{\rho}_{SE} - \mathcal{P}\hat{\rho}_{SE} \quad (2.7)$$

Here,  $\hat{\rho}_E$  is some fixed time independent state of the environment, not necessarily  $\text{Tr}_S\{\hat{\rho}_{SE}\}$ .

In the TCL formalism,  $\mathcal{P}$  is interpreted as a projector on a part of the full state space that is of interest to us, while  $\mathcal{Q}$  projects into the complement. Hence, given any potentially correlated SE state  $\hat{\rho}_{SE}(t)$ ,  $\mathcal{P}$  gets rid of the SE correlations and resets the environment to the fixed state  $\hat{\rho}_E$ . Note that this is *not* an assumption of the TCL formalism because we can always choose a projector  $\mathcal{P}$  with such a behaviour. Still, the following physical motivation can be given for the choice of the projector  $\mathcal{P}$ . We usually assume the environment to be a ‘large’ thermal system, initially, and we set  $\hat{\rho}_E$  to be this initial state of the environment, so in the weak coupling limit, the ‘small’ system is not able to significantly affect the dynamics of the environment. Hence, at a later time  $t$ , the state of the environment,  $\hat{\rho}_E(t)$ , can be assumed to be close to its initial state,  $\hat{\rho}_E$ . Moreover, the SE correlations and the small dynamical changes in the state of the environment are captured by the  $\mathcal{Q}$  operator, whose contribution to the dynamics is perturbatively added in the TCL formalism, as we will see in the subsequent discussion.

Next, we will make the following physically motivated assumption: odd moments of the interaction Hamiltonian with respect to  $\hat{\rho}_E$  vanish. That is, for any system state  $\hat{\rho}_S$ , we have

$$\text{Tr}_E \{ \hat{H}_I(t_1) \hat{H}_I(t_2) \dots \hat{H}_I(t_{2n+1}) (\hat{\rho}_S \otimes \hat{\rho}_E) \} = 0 \quad (2.8)$$

The physical motivation for this assumption is this. It is possible to express a general  $\hat{H}_I(t)$  as

$$\hat{H}_I(t) = \sum_i \hat{A}_i(t) \otimes \hat{B}_i(t) \quad (2.9)$$

where  $\hat{A}_i(t)$  and  $\hat{B}_i(t)$  are system and environment operators respectively. Then, if we assume the environment to be a collection of uncoupled harmonic oscillators in thermal state  $\hat{\rho}_E = e^{-\beta \hat{H}_E} / Z_E$  and  $\hat{B}_i(t)$  is linear in creation and annihilation operators for the  $i$ th environment oscillator mode, we can see that the odd moments of  $\hat{B}_i(t)$  vanish.

This result directly gives rise to

$$\mathcal{P}\mathcal{L}(t_1)\mathcal{L}(t_2)\dots\mathcal{L}(t_{2n+1})\mathcal{P}\hat{\rho}_{SE} = \mathcal{P}[\mathcal{L}(t_1)\mathcal{L}(t_2)\dots\mathcal{L}(t_{2n+1})\mathcal{P}\hat{\rho}_{SE}] \quad (2.10)$$

$$= \text{Tr}_E \{ \mathcal{L}(t_1)\mathcal{L}(t_2)\dots\mathcal{L}(t_{2n+1})\mathcal{P}\hat{\rho}_{SE} \} \otimes \hat{\rho}_E \quad (2.11)$$

$$= \text{Tr}_E \{ \mathcal{L}(t_1)\mathcal{L}(t_2)\dots\mathcal{L}(t_{2n+1}) \text{Tr}_E \{ \hat{\rho}_{SE} \} \otimes \hat{\rho}_E \} \otimes \hat{\rho}_E \quad (2.12)$$

$$= 0 \quad (2.13)$$

$$\implies \mathcal{P}\mathcal{L}(t_1)\mathcal{L}(t_2)\dots\mathcal{L}(t_{2n+1})\mathcal{P} = 0 \quad (2.14)$$

This result will be useful later for the simplification of the perturbative TCL expansions.

From the von Neumann equation in the interaction picture (Eq. (2.4)), we next write

$$\frac{\partial}{\partial t} \mathcal{P}\hat{\rho}_{SE}(t) = \mathcal{P} \frac{\partial}{\partial t} \hat{\rho}_{SE}(t) = \lambda \mathcal{P}\mathcal{L}(t)\hat{\rho}_{SE}(t) \quad (2.15)$$

$$\frac{\partial}{\partial t} \mathcal{Q}\hat{\rho}_{SE}(t) = \mathcal{Q} \frac{\partial}{\partial t} \hat{\rho}_{SE}(t) = \lambda \mathcal{Q}\mathcal{L}(t)\hat{\rho}_{SE}(t) \quad (2.16)$$

Here, we were able to write  $\partial_t \mathcal{P} = \mathcal{P} \partial_t$  because partial trace and partial derivative commute. Same for the  $\mathcal{Q}$  operator. Next, straightforward algebraic manipulation gives us:

$$\frac{\partial}{\partial t} \mathcal{P}\hat{\rho}_{SE}(t) = \lambda \mathcal{P}\mathcal{L}(t)(\mathcal{Q} + \mathcal{P})\hat{\rho}_{SE}(t) \quad (2.17)$$

$$= \lambda \mathcal{P}\mathcal{L}(t)\mathcal{P}\hat{\rho}_{SE}(t) + \lambda \mathcal{P}\mathcal{L}(t)\mathcal{Q}\hat{\rho}_{SE}(t) \quad (2.18)$$

Similarly, we have

$$\frac{\partial}{\partial t} \mathcal{Q}\hat{\rho}_{SE}(t) = \lambda \mathcal{Q}\mathcal{L}(t)\mathcal{P}\hat{\rho}_{SE}(t) + \lambda \mathcal{Q}\mathcal{L}(t)\mathcal{Q}\hat{\rho}_{SE}(t). \quad (2.19)$$

We need to solve Eq. (2.19) for  $\mathcal{Q}\hat{\rho}_{SE}(t)$  and insert the result into Eq. (2.18). To do so, we use the following proposition.

**Proposition 1.** Consider operators  $\hat{o}_i(t)$  that satisfy the coupled first-order equations

$$\frac{\partial}{\partial t} \hat{o}_i(t) = \lambda \sum_j \mathcal{A}_{ij}(t) \hat{o}_j(t). \quad (2.20)$$

Here,  $\mathcal{A}_{ij}(t)$  are superoperators. Then it can be proven that:

$$\hat{o}_i(t) = \mathcal{B}_i(t, 0) \hat{o}_i(0) + \lambda \int_0^t ds \mathcal{B}_i(t, s) \sum_{j \neq i} \mathcal{A}_{ij}(s) \hat{o}_j(s), \quad (2.21)$$

with the propagator defined as:

$$\mathcal{B}_i(t, s) \equiv \mathcal{T}_\leftarrow \exp \left[ \lambda \int_s^t ds' \mathcal{A}_{ii}(s') \right]. \quad (2.22)$$

where  $\mathcal{T}_\leftarrow$  denotes the chronological time-ordering operator.

*Proof.* Starting from Eq. (2.20), we write

$$\hat{o}_i(t) = \hat{o}_i(0) + \lambda \int_0^t dt_1 \mathcal{A}_{ii}(t_1) \hat{o}_i(t_1) + \lambda \int_0^t dt_1 \sum_{j \neq i} \mathcal{A}_{ij}(t_1) \hat{o}_j(t_1) \quad (2.23)$$

Next, let us replace  $\hat{o}_i(t_1)$  in the second term on the RHS using the expression for  $\hat{o}_i(t)$  given by the same equation (on the LHS). We will then keep on repeating this procedure for the new terms of the form  $\mathcal{A}_{ii}(t_k) \hat{o}_i(t_k)$  on the RHS for natural numbers  $k$ . Iterative performance of this procedure will give terms higher and higher in orders of  $\lambda$ .

That is, at the  $k$  operation of such a replacement, we will have (up to first order in  $\lambda$ )

$$\begin{aligned} \mathcal{A}_{ii}(t_k) \hat{o}_i(t_k) &\rightarrow \mathcal{A}_{ii}(t_k) \hat{o}_i(0) + \lambda \mathcal{A}_{ii}(t_k) \int_0^{t_k} dt_{k+1} \mathcal{A}_{ii}(t_{k+1}) \hat{o}_i(t_{k+1}) + \\ &\quad \lambda \mathcal{A}_{ii}(t_k) \int_0^{t_k} dt_{k+1} \sum_{j \neq i} \mathcal{A}_{ij}(t_{k+1}) \hat{o}_j(t_{k+1}). \end{aligned} \quad (2.24)$$

Since the second term on the RHS of Eq. (2.24) always get replaced, in the end, there will only two types of terms remaining, those of the form  $\mathcal{A}_{ii}(s) \hat{o}_i(0)$  and  $\mathcal{A}_{ij}(s) \hat{o}_j(s)$  for

$j \neq i$ . That is, terms that look like the first and the third term on the RHS of Eq. (2.24). If we collect all the terms that are of the first type, we get

$$\left[ 1 + \lambda \int_0^t dt_1 \mathcal{A}_{ii}(t_1) + \lambda^2 \int_0^t dt_1 \mathcal{A}_{ii}(t_1) \int_0^{t_1} dt_2 \mathcal{A}_{ii}(t_2) + \dots \right] \hat{\sigma}_i(0) = \mathcal{B}_i(t, 0) \hat{\sigma}_i(0). \quad (2.25)$$

Similarly, for a given  $s$ , if we collect all the terms that look like  $\mathcal{A}_{ij}(s) \hat{\sigma}_j(s)$  for  $j \neq i$ , we get

$$\int_0^t ds \left[ 1 + \lambda \int_s^t dt_1 \mathcal{A}_{ii}(t_1) + \lambda^2 \int_s^t dt_1 \mathcal{A}_{ii}(t_1) \int_s^{t_1} dt_2 \mathcal{A}_{ii}(t_2) + \dots \right] \sum_{j \neq i} \mathcal{A}_{ij}(s) \hat{\sigma}_j(s) = \int_0^t ds \mathcal{B}_i(t, s) \sum_{j \neq i} \mathcal{A}_{ij}(s) \hat{\sigma}_j(s). \quad (2.26)$$

Combined, these provide us the final result (Eq. (2.21)).  $\square$

In Eq. (2.19), we can use Proposition 1 by identifying  $\hat{\sigma}_1(t) \equiv Q\hat{\rho}_{SE}(t)$  and  $\hat{\sigma}_2(t) \equiv \mathcal{P}\hat{\rho}_{SE}(t)$ ,  $\mathcal{A}_{11}(t) \equiv Q\mathcal{L}(t)$  and  $\mathcal{A}_{12}(t) \equiv Q\mathcal{L}(t)$  to obtain:

$$Q\hat{\rho}_{SE}(t) = \mathcal{G}(t, 0) Q\hat{\rho}_{SE}(0) + \lambda \int_0^t ds \mathcal{G}(t, s) Q\mathcal{L}(s) \mathcal{P}\hat{\rho}_{SE}(s). \quad (2.27)$$

where, we have

$$\mathcal{G}(t, s) \equiv \mathcal{T}_{\leftarrow} \exp \left[ \lambda \int_s^t ds' Q\mathcal{L}(s') \right] \quad (2.28)$$

Next, to simplify this expression, we make a common assumption that the initial system environment state is uncorrelated, i.e.,

$$\hat{\rho}_{SE}(0) = \hat{\rho}_S(0) \otimes \hat{\rho}_E \implies Q\hat{\rho}_{SE}(0) = 0. \quad (2.29)$$

Also, we can use the property that

$$Q\mathcal{L}(s)\mathcal{P} = (\mathcal{I} - \mathcal{P})\mathcal{L}(s)\mathcal{P} \quad (2.30)$$

$$= \mathcal{L}(s)\mathcal{P} - \mathcal{P}\mathcal{L}(s)\mathcal{P} \quad (2.31)$$

$$= \mathcal{L}(s)\mathcal{P} \quad (\text{using } \mathcal{P}\mathcal{L}(s)\mathcal{P} = 0 \text{ from Eq. (2.14)}) \quad (2.32)$$

Both these results give us a simplified expression for Eq. (2.27) as

$$Q\hat{\rho}_{SE}(t) = \lambda \int_0^t ds \mathcal{G}(t, s) \mathcal{L}(s) \mathcal{P} \hat{\rho}_{SE}(s). \quad (2.33)$$

**Towards time-local master equation:** We *could* substitute Eq. (2.27) into Eq. (2.18) to obtain an equation for  $\mathcal{P}\hat{\rho}_{SE}(t)$  in terms of  $\mathcal{P}\hat{\rho}_{SE}(s)$ . However, this equation would have an explicit history dependence through  $\hat{\rho}_{SE}(s)$ , which we may want to avoid in certain cases. A time-local master equation, if possible, is ‘nice to have’ in the sense that we only need the current state of the system to predict its rate of change.

To obtain such a time-local equation for  $\mathcal{P}\hat{\rho}_{SE}(t)$ , we proceed as follows. Let us first define:

$$\hat{\rho}_{SE}(t) = G(t, s)(\mathcal{P} + \mathcal{Q})\hat{\rho}_{SE}(s). \quad (2.34)$$

with

$$G(t, s) \equiv \mathcal{T}_{\rightarrow} \exp \left[ -\lambda \int_s^t ds' \mathcal{L}(s') \right]. \quad (2.35)$$

Here,  $\mathcal{T}_{\rightarrow}$  denotes the anti-chronological time-ordering operator. Since we are talking about evolution of the global density matrix with unitary evolution, this back in time evolution is well-defined.

Using this in Eq. (2.33), we have

$$Q\hat{\rho}_{SE}(t) = \lambda \int_0^t ds \mathcal{G}(t, s) \mathcal{L}(s) \mathcal{P} G(t, s)(\mathcal{P} + \mathcal{Q})\hat{\rho}_{SE}(s). \quad (2.36)$$

This step took us one step backwards, because now we have an explicit dependence on  $Q\hat{\rho}_{SE}(t)$  on the RHS. To get rid of this dependence, we next define the super-operator

$$\Sigma(t) \equiv \lambda \int_0^t ds \mathcal{G}(t, s) \mathcal{L}(s) \mathcal{P} G(t, s), \quad (2.37)$$

so that Eq. (2.36) becomes:

$$[1 - \Sigma(t)] Q\hat{\rho}_{SE}(t) = \Sigma(t) \mathcal{P} \hat{\rho}_{SE}(t). \quad (2.38)$$

Let us assume that the operator norm of  $\Sigma(t)$  is less than 1, which ensures that  $1 - \Sigma(t)$  is invertible. This is guaranteed for sufficiently small values of  $t$  given any value of  $\lambda$  and vice versa. Then, we can solve for  $Q\hat{\rho}_{SE}(t)$  as

$$Q\hat{\rho}_{SE}(t) = [1 - \Sigma(t)]^{-1} \Sigma(t) \mathcal{P} \hat{\rho}_{SE}(t). \quad (2.39)$$

We can *now* substitute Eq. (2.39) into Eq. (2.18) to obtain a time-local master equation

$$\frac{\partial}{\partial t} \mathcal{P} \hat{\rho}_{SE}(t) = \lambda \mathcal{P} \mathcal{L}(t) \mathcal{P} \hat{\rho}_{SE}(t) + \lambda \mathcal{P} \mathcal{L}(t) ([1 - \Sigma(t)]^{-1} \Sigma(t) \mathcal{P} \hat{\rho}_{SE}(t)), \quad (2.40)$$

$$= \lambda \mathcal{P} \mathcal{L}(t) ((1 + [1 - \Sigma(t)]^{-1} \Sigma(t)) \mathcal{P} \hat{\rho}_{SE}(t)), \quad (2.41)$$

$$= \lambda \mathcal{P} \mathcal{L}(t) \left( \frac{1 - \Sigma(t)}{1 - \Sigma(t)} + \frac{\Sigma(t)}{1 - \Sigma(t)} \right) \mathcal{P} \hat{\rho}_{SE}(t), \quad (2.42)$$

$$= \lambda \mathcal{P} \mathcal{L}(t) [1 - \Sigma(t)]^{-1} \mathcal{P} \hat{\rho}_{SE}(t), \quad (2.43)$$

$$\implies \frac{\partial}{\partial t} \mathcal{P} \hat{\rho}_{SE}(t) = \mathcal{F}(t) \mathcal{P} \hat{\rho}_{SE}(t). \quad (2.44)$$

This is the TCL master equation for factorized initial states, with the TCL generator  $\mathcal{F}(t)$  defined as

$$\mathcal{F}(t) \equiv \lambda \mathcal{P} \mathcal{L}(t) [1 - \Sigma(t)]^{-1} \mathcal{P}. \quad (2.45)$$

We can now perturbatively expand the TCL generator  $\mathcal{F}(t)$  in powers of  $\lambda$ . We first use,

$$[1 - \Sigma(t)]^{-1} = \sum_{n=0}^{\infty} [\Sigma(t)]^n. \quad (2.46)$$

**Disappearance of odd order terms in TCL:** To perturbatively evaluate the TCL2n generator, we can write

$$\Sigma(t) = \sum_{n=1}^{\infty} \lambda^n \Sigma_n(t), \quad (2.47)$$

$$\mathcal{F}(t) = \sum_{n=1}^{\infty} \lambda^n \mathcal{F}^{(n)}(t). \quad (2.48)$$

In both the above expressions, we note that the summation starts from  $n = 1$  rather than  $n = 0$ , which follows from their definitions (Eqs. (2.37) and (2.45)). Here,  $\Sigma_n(t)$  are obtained by expanding the exponentials in Eq. (2.37) (which are  $\mathcal{G}(t, s)$  and  $G(t, s)$ ) and collecting equal powers of  $\lambda$ . Similarly,  $\mathcal{F}^{(n)}(t)$  are obtained by replacing Eq. (2.46) in Eq. (2.45) and collecting equal powers of  $\lambda$ .

Before proceeding, we will motivate why the odd order terms in the expansion of  $\mathcal{F}(t)$  vanish. This is because the expression of  $\mathcal{F}(t)$  (Eq. (2.45)) can be expressed as nested integrals in time, where each integrand has the following symbolic form:

$$\mathcal{P}\mathcal{L}(t_{11})\mathcal{L}(t_{12})\mathcal{L}(t_{13})\dots\mathcal{P}\mathcal{L}(t_{21})\mathcal{L}(t_{22})\dots\mathcal{P}\dots\mathcal{L}(t_{n1})\mathcal{L}(t_{n2})\dots\mathcal{P}. \quad (2.49)$$

Here, each index  $t_{ij}$  is a time variable, which, if necessary, is also integrated over. These extra time variables appear as dummy variables when we expand  $\mathcal{G}(t, s)$  and  $G(t, s)$  in the expression of  $\Sigma(t)$  (Eq. (2.37)). We emphasize that by claiming that  $\mathcal{F}(t)$  will have integrand of the form Eq. (2.49), all we are saying is that the terms will have  $\mathcal{L}$  operators sandwiched by  $\mathcal{P}$  (which follows from expression of  $\mathcal{F}(t)$  (Eq. (2.45))), with perhaps multiple  $\mathcal{P}$  in the middle of the expression.

We can then use the fact that the odd order moments vanish (see Eq. (2.14)) to prove that

any such term like  $\mathcal{P}\mathcal{L}(t_{i1})\mathcal{L}(t_{i2})\mathcal{L}(t_{i3})\dots\mathcal{P}$  will have even number of operators  $\mathcal{L}$ , hence proving that overall, each nonvanishing term will also have even number of operators  $\mathcal{L}$ . Since each  $\mathcal{L}$  carries with it a factor of  $\lambda$ , this means that all odd order terms in the expansion of  $\mathcal{F}(t)$  will vanish, and only even order terms will survive.

**Perturbative expansion of the TCL generator:** In the perturbative expansion of  $\mathcal{F}(t)$  (Eq. (2.48)), collecting equal powers of  $\lambda$  gives

$$\mathcal{F}^{(2)}(t) = \mathcal{P}\mathcal{L}(t)\Sigma_1(t)\mathcal{P}, \quad (2.50)$$

$$\mathcal{F}^{(4)}(t) = \mathcal{P}\mathcal{L}(t) \left( [\Sigma_1(t)]^3 + \Sigma_1(t)\Sigma_2(t) + \Sigma_2(t)\Sigma_1(t) + \Sigma_3(t) \right) \mathcal{P}. \quad (2.51)$$

The first few  $\Sigma_n(t)$  follow from Eq. (2.37) by also expanding the propagators:

$$\Sigma_1(t) = \int_0^t dt_1 \mathcal{L}(t_1)\mathcal{P}, \quad (2.52)$$

$$\Sigma_2(t) = \int_0^t dt_1 \int_0^{t_1} dt_2 [\mathcal{Q}\mathcal{L}(t_1)\mathcal{L}(t_2)\mathcal{P} - \mathcal{L}(t_2)\mathcal{P}\mathcal{L}(t_1)]. \quad (2.53)$$

$$\begin{aligned} \Sigma_3(t) = \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 & \mathcal{Q}\mathcal{L}(t_1)\mathcal{Q}\mathcal{L}(t_2)\mathcal{L}(t_3)\mathcal{P} - \mathcal{Q}\mathcal{L}(t_1)\mathcal{L}(t_3)\mathcal{P}\mathcal{L}(t_2) \\ & - \mathcal{Q}\mathcal{L}(t_2)\mathcal{L}(t_3)\mathcal{P}\mathcal{L}(t_1) + \mathcal{L}(t_3)\mathcal{P}\mathcal{L}(t_2)\mathcal{L}(t_1) \end{aligned} \quad (2.54)$$

**Explicit forms of TCL2 generator:** Using  $\mathcal{P}\mathcal{Q} = 0$  and the vanishing of all odd environment moments (see Eq. (2.14)), we obtain

$$\mathcal{F}^{(2)}(t) = \int_0^t dt_1 \mathcal{P}\mathcal{L}(t)\mathcal{L}(t_1)\mathcal{P}, \quad (2.55)$$

Using the definitions of  $\mathcal{L}$  and  $\mathcal{P}$  (Eqs. (2.5) and (2.6)), this gives us the TCL2 master equation as

$$\mathcal{F}^{(2)}(t)\hat{\rho}_S(t) = \int_0^t dt_1 \mathcal{P}\mathcal{L}(t)\mathcal{L}(t_1)(\hat{\rho}_S(t) \otimes \hat{\rho}_E) \quad (2.56)$$

$$= - \int_0^t dt_1 \text{Tr}_E[\hat{H}_I(t), [\hat{H}_I(t_1), \hat{\rho}_S(t) \otimes \hat{\rho}_E]] \quad (2.57)$$

For the purpose of this thesis, we will assume that  $\hat{H}_I(t)$  (Eq. (2.9)) can be written as

$$\hat{H}_I(t) = \hat{A}(t) \otimes \hat{B}(t). \quad (2.58)$$

The general treatment (Eq. (2.9)) can likewise be done. For our convenience, let us define the real and imaginary parts of the environment two-point correlation functions as:

$$\nu(t_1, t_2) = \Re \text{Tr}_E \{ \hat{B}(t_1) \hat{B}(t_2) \hat{\rho}_E \}, \quad (2.59)$$

$$\eta(t_1, t_2) = \Im \text{Tr}_E \{ \hat{B}(t_1) \hat{B}(t_2) \hat{\rho}_E \}, \quad (2.60)$$

We can now insert Eqs. (2.58) to (2.60) into Eq. (2.56) to obtain:

$$\mathcal{F}^{(2)}(t) \hat{\rho}_S(t) = - \int_0^t dt_1 (\nu_{01} [\hat{0}, [\hat{1}, \hat{\rho}_S(t)]] + i\eta_{01} [\hat{0}, \{\hat{1}, \hat{\rho}_S(t)\}]). \quad (2.61)$$

Here, we have used the shorthand notation  $\hat{i} \equiv \hat{A}(t_i)$  with  $t_0 \equiv t$  and likewise  $\nu_{ij} \equiv \nu(t_i, t_j)$  and  $\eta_{ij} \equiv \eta(t_i, t_j)$ .

**Explicit forms of TCL4 generator:** We can similarly solve for TCL4 generator as:

$$\begin{aligned} \mathcal{F}^{(4)}(t) = \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \bigg\{ & \mathcal{P} \mathcal{L}(t) \mathcal{L}(t_1) \mathcal{L}(t_2) \mathcal{L}(t_3) \mathcal{P} - \mathcal{P} \mathcal{L}(t) \mathcal{L}(t_1) \mathcal{P} \mathcal{L}(t_2) \mathcal{L}(t_3) \mathcal{P} \\ & - \mathcal{P} \mathcal{L}(t) \mathcal{L}(t_2) \mathcal{P} \mathcal{L}(t_1) \mathcal{L}(t_3) \mathcal{P} - \mathcal{P} \mathcal{L}(t) \mathcal{L}(t_3) \mathcal{P} \mathcal{L}(t_1) \mathcal{L}(t_2) \mathcal{P} \bigg\} \end{aligned} \quad (2.62)$$

When we try to evaluate  $\mathcal{P} \mathcal{L}(t) \mathcal{L}(t_1) \mathcal{L}(t_2) \mathcal{L}(t_3) \mathcal{P} \hat{\rho}_{SE}$ , we get 4-point correlation functions of the environment operators of the form  $\text{Tr}_E \{ \hat{B}(t_i) \hat{B}(t_j) \hat{B}(t_k) \hat{B}(t_l) \hat{\rho}_E \}$ . Assuming that the environment is in a Gaussian state (which is the case for thermal states of harmonic oscillator environments) and  $\hat{B}(t)$  is linear in creation and annihilation operators of the environment modes, we can use Wick's theorem to express these 4-point correlation functions in terms of the 2-point correlation functions as:

$$\text{Tr}_E \{ \hat{B}(t_0) \hat{B}(t_1) \hat{B}(t_2) \hat{B}(t_3) \hat{\rho}_E \} = \text{Tr}_E \{ \hat{B}(t_0) \hat{B}(t_1) \hat{\rho}_E \} \text{Tr}_E \{ \hat{B}(t_2) \hat{B}(t_3) \hat{\rho}_E \}$$

$$\begin{aligned}
& + \text{Tr}_E \{ \hat{B}(t_0) \hat{B}(t_2) \hat{\rho}_E \} \text{Tr}_E \{ \hat{B}(t_1) \hat{B}(t_3) \hat{\rho}_E \} \\
& + \text{Tr}_E \{ \hat{B}(t_0) \hat{B}(t_3) \hat{\rho}_E \} \text{Tr}_E \{ \hat{B}(t_1) \hat{B}(t_2) \hat{\rho}_E \} \quad (2.63)
\end{aligned}$$

In the Supplementary Material [52], we have provided the detailed symbolic calculation, using Mathematica, to reduce Eq. (2.62) to the final form as:

$$\begin{aligned}
\mathcal{F}^{(4)}(t) \hat{\rho}_S = & \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \\
& \times \left( \nu_{02} \nu_{13} [\hat{0}, [[\hat{1}, \hat{2}], [\hat{3}, \hat{\rho}_S]]] + i \nu_{02} \eta_{13} [\hat{0}, [[\hat{1}, \hat{2}], \{\hat{3}, \hat{\rho}_S\}]] \right. \\
& + i \eta_{02} \nu_{13} [\hat{0}, \{\{\hat{1}, \hat{2}\}, [\hat{3}, \hat{\rho}_S]\}] - \eta_{02} \eta_{13} [\hat{0}, \{\{\hat{1}, \hat{2}\}, \{\hat{3}, \hat{\rho}_S\}\}] \\
& + \nu_{03} \nu_{12} [\hat{0}, [[\hat{1}, \hat{3}], [\hat{2}, \hat{\rho}_S]]] + i \nu_{03} \eta_{12} [\hat{0}, [[\hat{1}, \hat{3}], \{\hat{2}, \hat{\rho}_S\}]] \\
& + i \eta_{03} \nu_{12} [\hat{0}, \{\{\hat{1}, \hat{3}\}, [\hat{2}, \hat{\rho}_S]\}] - \eta_{03} \eta_{12} [\hat{0}, \{\{\hat{1}, \hat{3}\}, \{\hat{2}, \hat{\rho}_S\}\}] \\
& + (\nu_{03} \nu_{12} - \eta_{03} \eta_{12}) [\hat{0}, [\hat{1}, [[\hat{2}, \hat{3}], \hat{\rho}_S]]] \\
& \left. + i(\nu_{03} \eta_{12} + \eta_{03} \nu_{12}) [\hat{0}, [\hat{1}, \{\{\hat{2}, \hat{3}\}, \hat{\rho}_S\}]] \right) \quad (2.64)
\end{aligned}$$

### 2.1.2 The Steady State of Time-Convolutionless Master Equation

In this section, we discuss the perturbative corrections to the SS of the TCL master equation [9, 88]. Back in the Schrodinger picture, the TCL-ME in Eq. (2.44) can be formally written as

$$\dot{\hat{\rho}}_S(t) = \sum_{n=0}^{\infty} \lambda^{2n} \mathcal{F}^{(2n)}(t) [\hat{\rho}(t)], \quad (2.65)$$

where, the  $\mathcal{F}^{(2n)}$  for  $n \geq 1$  is now the schrodinger picture version of the TCL generator and  $\mathcal{F}^{(0)}$  is the free evolution generator. Let us define the asymptotic limit of the TCL  $2n$  generator as

$$\mathcal{F}^{(2n)} = \lim_{t \rightarrow \infty} \mathcal{F}^{(2n)}(t). \quad (2.66)$$

We remark that the asymptotic limit of a TCL generator does not exist if the environment two-point correlation functions (Eqs. (2.59) and (2.60)) decay algebraically in the long time limit [12]. In this thesis, though, we will see later that the assumptions we make lead to the environment correlation functions decaying exponentially, hence the asymptotic limit exists. See Sec. 3.3.2 for more details.

The perturbative expression for the steady state (SS)  $\hat{\rho}_{SS}$  of the TCL-ME can be obtained by solving

$$(\mathcal{F}^{(0)} + \lambda^2 \mathcal{F}^{(2)} + \dots) [\hat{\rho}^{(0)} + \lambda^2 \hat{\rho}^{(2)} + \dots] = 0. \quad (2.67)$$

Here,  $\hat{\rho}^{(0)}$  is the Gibbs state and the higher order terms are corrections over it.

We note that for any state diagonal in the system free Hamiltonian  $\hat{H}_S$ , we have

$$\mathcal{F}^{(0)}[\hat{\rho}_{\text{diag}}] = -i[\hat{H}_S, \hat{\rho}_{\text{diag}}] = 0. \quad (2.68)$$

This means that  $\mathcal{F}^{(0)}$  has degeneracy, and we need one order higher in the perturbation theory to lift this degeneracy. Hence, we need  $TCL(2n + 2)$  in order to obtain the  $2n$ -th order corrections to the diagonal part of the SS [9].

For example, the zeroth order expression from Eq. (2.67),

$$\mathcal{F}^{(0)}[\hat{\rho}^{(0)}] = -i[\hat{H}_S, \hat{\rho}^{(0)}] = 0. \quad (2.69)$$

tells us that  $\hat{\rho}^{(0)}$  is diagonal in the energy eigenbasis of  $\hat{H}_S$ . The second order expression from Eq. (2.67):

$$\mathcal{F}^{(0)}[\hat{\rho}^{(2)}] + \mathcal{F}^{(2)}[\hat{\rho}^{(0)}] = 0, \quad (2.70)$$

gives us the actual values of the diagonal elements of  $\hat{\rho}^{(0)}$  (i.e., the Gibbs state popula-

tions) and the off-diagonal elements of  $\hat{\rho}^{(2)}$  (i.e., the 2nd order coherences). Consequently, to get the 2nd order SS population and the 4th order SS coherences, we need the 4th order expression from Eq. (2.67):

$$\mathcal{F}^{(0)}[\hat{\rho}^{(4)}] + \mathcal{F}^{(2)}[\hat{\rho}^{(2)}] + \mathcal{F}^{(4)}[\hat{\rho}^{(0)}] = 0. \quad (2.71)$$

And so on and so forth for higher order corrections.

## 2.2 The Spin-Boson model

In this thesis, the TCL formalism will be applied to a specific open quantum system model called the Spin-Boson Model (SBM). We review the SBM briefly in this section.

The SBM consists of a two level quantum system coupled to several Bosonic modes, uncoupled from each other [3, 4]. It is a powerful model that has found wide scale applications in diverse fields from quantum chemistry and biology to many body physics and quantum information, computing, and technology. For example, the SBM has been used to study bio-molecule systems like chromophores and photosynthetic complexes [34–36], trapped ions [7], electron transfer reactions [37, 38] and superconducting circuits [6].

The general Hamiltonian for the SBM is given as [3, 4]

$$\hat{H}_S \equiv \frac{\Omega}{2} \hat{\sigma}_3, \quad (2.72)$$

$$\hat{H}_E = \sum_k \left[ \frac{\hat{p}_k^2}{2m_k} + \frac{1}{2} m_k \omega_k^2 \hat{q}_k^2 \right] \quad (2.73)$$

where,  $\hat{p}_k$  and  $\hat{q}_k$  are the momentum and position operators of the  $k$ th Bosonic oscillator with mass  $m_k$ , frequency  $\omega_k$  and SE coupling strength  $c_k$ . For the purpose of this thesis, we assume that the system and environment component of the interaction Hamiltonian

( $\hat{H}_I \equiv \lambda \hat{A} \otimes \hat{B}$ , see Eq. (2.58)) is given as

$$\hat{A} = a_3 \hat{\sigma}_3 - a_1 \hat{\sigma}_1, \quad (2.74)$$

$$\hat{B} = \sum_k c_k \hat{q}_k, \quad (2.75)$$

where  $\hat{\sigma}_i$  is the Pauli matrix. We remark that  $\hat{\sigma}_2$  component of the system operator  $\hat{A}$  is absent without any loss of generality. This is because Pauli matrices are associated with specific directions in the physical space, and we can always choose new basis for the  $x$  and  $y$  directions in this particular case to get rid of the  $\hat{\sigma}_2$  component in  $\hat{A}$ . Throughout this work, unless otherwise mentioned, we have chosen  $a_1 = \sin(\theta)$  and  $a_3 = \cos(\theta)$ .

### 2.2.1 Bath correlation functions

Now we are in a position to exactly calculate the bath correlation functions  $\nu(t_1, t_2)$  and  $\eta(t_1, t_2)$  (see Eq. (2.59) and Eq. (2.60)), which, as we have seen, are required to compute the TCL generators. We are interested in calculating:

$$\langle \hat{B}(t_1) \hat{B}(t_2) \rangle = \text{Tr}_E \{ \hat{B}(t_1) \hat{B}(t_2) \hat{\rho}_E \}, \quad (2.76)$$

$$= \sum_{k, k'} c_k c_{k'} \text{Tr}_E \{ \hat{q}_k(t_1) \hat{q}_{k'}(t_2) \hat{\rho}_E \}, \quad (2.77)$$

$$= \sum_k c_k^2 \text{Tr}_E \{ \hat{q}_k(t_1) \hat{q}_k(t_2) \hat{\rho}_E \} \quad (2.78)$$

Here, we have assumed that the environment oscillators are initially uncoupled from each other and in their respective thermal states. Hence, for  $k \neq k'$ ,  $\text{Tr}_E \{ \hat{q}_k(t_1) \hat{q}_{k'}(t_2) \hat{\rho}_E \} = \langle \hat{q}_k(t_1) \rangle \langle \hat{q}_{k'}(t_2) \rangle = 0$ . Here, we have also used the fact that odd order moments of an operator linear in creation and annihilation operators vanish for a thermal state (Eq. (2.14)).

Let us first evaluate the two point correlation function  $\langle \hat{q}(t_1) \hat{q}(t_2) \rangle$  for a single harmonic

oscillator mode with frequency  $\omega$  at inverse temperature  $\beta$ . This is given as

$$\langle \hat{q}(t_1) \hat{q}(t_2) \rangle = \frac{1}{Z} \text{Tr} \left\{ e^{i\hat{H}t_1} \hat{q}(0) e^{i\hat{H}(t_2-t_1)} \hat{q}(0) e^{-i\hat{H}t_2} e^{-\beta\hat{H}} \right\}, \quad (2.79)$$

$$= \frac{1}{Z} \text{Tr} \left\{ \hat{q}(0) e^{i\hat{H}t} \hat{q}(0) e^{-i\hat{H}t} e^{-\beta\hat{H}} \right\}, \text{ for } t = t_2 - t_1 \quad (2.80)$$

$$= \frac{1}{2m\omega Z} \text{Tr} \left\{ (\hat{a} + \hat{a}^\dagger)(\hat{a}e^{-i\omega t} + \hat{a}^\dagger e^{i\omega t}) e^{-\beta\hat{H}} \right\}, \quad (2.81)$$

$$= \frac{1}{2m\omega} (\langle \hat{a}\hat{a}^\dagger \rangle e^{i\omega t} + \langle \hat{a}^\dagger\hat{a} \rangle e^{-i\omega t}), \quad (2.82)$$

$$= \frac{1}{2m\omega} \left( \coth\left(\frac{\beta\omega}{2}\right) \cos(\omega(t_1 - t_2)) - i \sin(\omega(t_1 - t_2)) \right). \quad (2.83)$$

Then, we can express the full bath correlation function as

$$\langle \hat{B}(t_1) \hat{B}(t_2) \rangle = \sum_k \frac{c_k^2}{2m_k\omega_k} \left[ \coth\left(\frac{\beta\omega_k}{2}\right) \cos(\omega_k(t_1 - t_2)) - i \sin(\omega_k(t_1 - t_2)) \right]. \quad (2.84)$$

Sometimes, it may be convenient to express the summation over the environment oscillators as an integral over a continuous frequency variable. For this purpose, we define the spectral density of the environment as follows.

$$J(\omega) \equiv \sum_k \frac{c_k^2}{2m_k\omega_k} \delta(\omega - \omega_k). \quad (2.85)$$

Using this definition, we can formally write the bath correlation function as

$$\langle \hat{B}(t_1) \hat{B}(t_2) \rangle = \int_0^\infty d\omega J(\omega) \left[ \coth\left(\frac{\beta\omega}{2}\right) \cos(\omega(t_1 - t_2)) - i \sin(\omega(t_1 - t_2)) \right]. \quad (2.86)$$

When there are a large number of environment oscillators with closely spaced frequencies, the spectral density  $J(\omega)$  can be approximated as a smooth function of frequency  $\omega$ .

### 2.2.2 Modelling physical open quantum systems with the SBM

Here, we briefly discuss how the SBM can be used to effectively model a physical open quantum system.

**The validity of the harmonic environment approximation:** Modeling the environment as a collection of harmonic oscillators may be exactly valid in some cases, while in other cases, it may be approximately valid in certain parameter regimes. Moreover, it might also be possible to use the Harmonic environment model as an effective phenomenological description of the environment [5]. Although, as discussed in Sec. 1.4, we do note that the harmonic environment model does fail in certain chemical systems [68–71, 75–78].

**The validity of the bilinear coupling approximation:** Motivation for the bilinear nature of the coupling of the system to a single environment mode can be found in classic textbooks [2, 4]. The argument goes as follows: for an environment with a large number of modes, the coupling to any single mode is expected to be weak, and hence can be approximated to be linear in the displacement of the oscillator corresponding to the mode from its equilibrium position. Note that this does not imply that the overall SE coupling is weak, as the system can be strongly coupled to the collective effect of several environment modes [4]. Also, the bilinear coupling between the SE operators can be thought of as arising from a classical spring-like interaction between the system and environment degrees of freedom [2]. That is, we can rewrite the SBM interaction Hamiltonian as

$$\hat{H}_I = \lambda \hat{A} \otimes \hat{B}, \quad (2.87)$$

$$= -\left(\hat{B} - \frac{\lambda}{2}\hat{A}\right)^2 + \hat{B}^2 + \frac{\lambda^2}{4}\hat{A}^2, \quad (2.88)$$

where  $\hat{B}^2$  and  $\lambda^2\hat{A}^2/4$  terms can be absorbed into the free Hamiltonians of the environment and system, respectively. We note here that Eq. (2.87) is a special case of the general Hamiltonian discussed before in Eq. (2.9).

**The form of the spectral density:** When physically modelling a specific system, the form of the spectral density  $J(\omega)$  can be either deduced from experimental data [89] or can be derived from a microscopic model of the environment [41, 44, 90–92]. Moreover, phenomenological toy model forms of  $J(\omega)$  that capture the essential physics of the system while remaining analytically and numerically tractable are also widely used in the literature. An example of one such phenomenological model is the Ohmic spectral density with Drude cutoff, which we utilize later in this thesis to benchmark our more-general TCL4 calculations.

The form of the Ohmic spectral density with Drude cutoff is given as

$$J_D(\omega) = \frac{\gamma\Lambda^2\omega}{\Lambda^2 + \omega^2}, \quad (2.89)$$

with coupling strength  $\gamma$  and frequency cutoff  $\Lambda$ . The frequency cutoff  $\Lambda$  physically represents the maximum frequency up to which the environment modes can effectively interact with the system. The corresponding bath correlators (Eqs. (2.59) and (2.60)) have closed forms given as [3]:

$$\eta_D(t) = -\frac{\pi}{2}\gamma\Lambda^2 e^{-\Lambda t}, \quad (2.90)$$

$$\nu_D(t) = \sum_{n=-\infty}^{\infty} \frac{\pi\gamma\Lambda^2(\Lambda e^{-\Lambda t} - |\mu_n|e^{-|\mu_n|t})}{\beta(\Lambda^2 - |\mu_n|^2)}, \quad (2.91)$$

where  $\mu_n = 2\pi n/\beta$  are Matsubara frequencies. The evaluation of the TCL4 generator can be carried out analytically for this choice of spectral density, as we will discuss in Sec. 3.4.5. This will serve as a benchmark to check the validity of our more general results for the special case of the Ohmic spectral density with Drude cutoff.

**Double Quantum Dot as Spin-Boson Model:** Here, we provide a simple description of a physical system that can be effectively modelled as a SBM. The system in question is a semiconductor double quantum dot (DQD), which we will use as a case study for our TCL calculations in Sec. 4.1. A semiconductor quantum dot can be thought of as a

fermionic particle confined in a box.

Although it is not directly related to the main results of this thesis, we provide a brief description of how such a system can be physically realized in a semiconductor environment, as discussed by Hanson et al. [93]. First, layers of Gallium Arsenide (GaAs) and Aluminum Gallium Arsenide (AlGaAs) are created with a 2D potential well at the interface, the latter being 50-100 nm wide. The AlGaAs layer is doped with Silicon atoms, creating free electrons that accumulate in the 2D potential well at the interface, forming a two-dimensional electron gas (2DEG). By applying negative voltages to metallic gates fabricated on top of the semiconductor heterostructure, small regions of the 2DEG can be depleted of electrons, effectively creating potential wells that can confine electrons in all three spatial dimensions. These confined regions are called quantum dots. In a DQD system, two such quantum dots are placed in close proximity to each other, allowing for tunneling of electrons between the dots. The background phonons in the semiconducting material can be modelled as a Bosonic environment coupled to the DQD system.

Purkayastha et al. provide the DQD Hamiltonian  $\hat{\mathcal{H}} = \hat{\mathcal{H}}_S + \hat{\mathcal{H}}_{SE} + \hat{\mathcal{H}}_E$  as [1]:

$$\hat{\mathcal{H}}_S = \frac{\epsilon}{2} (\hat{n}_1 - \hat{n}_2) + t_c (\hat{c}_1^\dagger \hat{c}_2 + \hat{c}_2^\dagger \hat{c}_1) + V \hat{n}_1 \hat{n}_2, \quad (2.92)$$

$$\hat{\mathcal{H}}_E = \sum_k \Omega_k \hat{b}_k^\dagger \hat{b}_k, \quad (2.93)$$

$$\hat{\mathcal{H}}_{SE} = \hat{B} (\hat{n}_1 - \hat{n}_2), \quad (2.94)$$

$$\hat{B} = \sum_k \lambda_k (\hat{b}_k^\dagger + \hat{b}_k) \quad (2.95)$$

Here  $\hat{n}_\ell = \hat{c}_\ell^\dagger \hat{c}_\ell$ ,  $\hat{c}_\ell$  is the fermionic annihilation operator of the  $\ell$ th site and  $\hat{b}_k$  is the phononic annihilation operator of the  $k$ th mode. Here, parameters of the model are the detuning  $\epsilon$ , inter-dot tunneling  $t_c$  and the repulsive interaction between the two sites is given by  $V$ . We note that the total Hamiltonian does not change the total number of electrons in the DQD system, i.e.,  $[\hat{\mathcal{H}}, \hat{n}_1 + \hat{n}_2] = 0$ . Purkayastha et al. use this fact and show that under the assumption of single occupancy of the DQD system (i.e.,  $\hat{n}_1 + \hat{n}_2 =$

1), the DQD Hamiltonian can be mapped to the SBM Hamiltonian. In our convention (Eq. (2.72)-Eq. (2.75)), this implies the following identifications:

$$a_1 = \frac{2t_c}{\Omega}, \quad (2.96)$$

$$a_3 = \frac{\epsilon}{\Omega}, \quad (2.97)$$

$$\Omega^2 = \epsilon^2 + 4t_c^2. \quad (2.98)$$

The DQD is coupled to the phononic bath, described by the spectral density [1]:

$$J(\omega) = \gamma\omega \left[ 1 - \text{sinc}\left(\frac{\omega}{\omega_c}\right) \right] \exp\left\{-\frac{\omega^2}{2\omega_{\max}^2}\right\}, \quad (2.99)$$

where, we have  $\text{sinc}(x) \equiv \sin(x)/x$ . This spectral density effectively describes the bulk acoustic phonons in Gallium Arsenide (GaAs) DQDs [1, 41, 42, 44]. The parameter  $\omega_{\max}$  serves as the upper cut-off frequency, while  $\omega_c = c_s/d$ , where  $c_s$  is the speed of sound in the substrate and  $d$  is the inter-dot distance. The term  $\gamma$  dictates the coupling strength between the DQD system and its phonon environment.

Following Purkayastha et al. [1, p. 3], we set the length unit to the inter-dot distance,  $L_0 = d = 150 \text{ nm}$ . Using their value  $c_s \simeq 3000 \text{ m/s}$  and  $\omega_c = c_s/d$ , the corresponding energy unit is  $E_0 = \hbar\omega_c = \hbar c_s/d \approx 2 \times 10^{-24} J$ .

### 2.2.3 Bloch-Vectorization

To simplify the TCL calculations, we will use the vectorized notation for the system state as following,

$$v_i(t) = \text{Tr}\{\hat{\sigma}_i \hat{\rho}_S(t)\}, \quad (2.100)$$

where the index  $i$  runs from 0 to 3.  $\hat{\sigma}_i$  are the Pauli matrices for  $i = 1, 2, 3$  and  $\hat{\sigma}_0$  is the identity matrix. Then the TCL-ME for this system can be written as [94],

$$\dot{\vec{v}}(t) = \sum_{n=0}^{\infty} \lambda^{2n} F^{(2n)}(t) \vec{v}(t), \quad (2.101)$$

where  $F^{(2n)}(t)$  is a  $4 \times 4$  matrix with matrix elements  $F_{jk}^{(2n)}(t)$  which can be obtained from the superoperator  $\mathcal{F}(t)$  (see Eq. (2.44)) as

$$F_{jk}^{(2n)}(t) \equiv \frac{1}{2} \text{Tr} \{ \hat{\sigma}_j \mathcal{F}^{(2n)}(t) [\hat{\sigma}_k] \}. \quad (2.102)$$

In the asymptotic limit, let us define

$$F_{jk}^{(2n)} \equiv \lim_{t \rightarrow \infty} F_{jk}^{(2n)}(t), \quad (2.103)$$

$$v_j \equiv \lim_{t \rightarrow \infty} v_j(t). \quad (2.104)$$

The components  $v_j$  have a perturbative expansion in  $\lambda^2$  as

$$v_j = v_j^{(0)} + \lambda^2 v_j^{(2)} + \lambda^4 v_j^{(4)} + \dots, \quad (2.105)$$

and can systematically be calculated order by order [3, 94], as we will show using TCL2 and TCL4 in Secs. 3.1 and 3.2. Here, we have taken the expansion in even powers of  $\lambda$  because the odd order contributions vanish for the SBM under the assumption of our model (Eq. (2.14)).

## 2.3 Non-Markovianity of Open Quantum System Dynamics

In this section, we briefly discuss some basic concepts related to open quantum systems that will help us define the notion of memory effects in the dynamics of such systems.

### 2.3.1 Physical Open Quantum System Maps

Let us denote the time evolution under a generic open quantum system as

$$\hat{\rho}_S(t) = \Phi_t[\hat{\rho}_S(0)], \quad (2.106)$$

Then, physical constraints on the evolution map  $\Phi_t$  are that it should be:

1. Trace preserving (TP), i.e.,  $\text{Tr} \{ \Phi_t[\hat{\rho}_S(0)] \} = \text{Tr} \{ \hat{\rho}_S(0) \}$ . This essentially ensures that the total probability is conserved under evolution.
2. Completely positive (CP), i.e., for any bipartite system  $S + S'$ , where  $S'$  is an arbitrary ancilla system, the map  $\Phi_t \otimes \mathbb{I}_{S'}$  should also be positive. This ensures that the evolution map does not lead to unphysical states when the system is correlated with an ancillary system.

We remark here that there exist positive maps that are not CP. One typical example of such map is the transpose map, whose action is as follows:

$$\hat{\rho}_{SS'} = \sum_{ijkl} \rho_{ijkl} |i\rangle_S \langle j| \otimes |k\rangle_{S'} \langle l| \xrightarrow{T_S \otimes \mathbb{I}_{S'}} \sum_{ijkl} \rho_{ijkl} |j\rangle_S \langle i| \otimes |k\rangle_{S'} \langle l|. \quad (2.107)$$

To show that the transpose map is not CP, let us consider its action on one half of a maximally entangled state  $|\Psi\rangle_{SS'} = \frac{1}{\sqrt{d}} \sum_{i=1}^d |i\rangle_S \otimes |i\rangle_{S'}$ , where  $d$  is the dimension of the

Hilbert space of system  $S$  and  $S'$ . The density matrix corresponding to this state is given as

$$\hat{\rho}_{SS'}^{(d)} = \frac{1}{d} \sum_{ijkl} |i\rangle_S \langle j| \otimes |i\rangle_{S'} \langle j|. \quad (2.108)$$

Now, applying the transpose map on system  $S$ , we get

$$\hat{\rho}'_{SS'}^{(d)} = \frac{1}{d} \sum_{ijkl} |j\rangle_S \langle i| \otimes |i\rangle_{S'} \langle j|. \quad (2.109)$$

For  $d = 2$ ,  $\hat{\rho}'_{SS'}^{(2)}$  can be explicitly expressed as following in the computational basis  $\{|00\rangle, |01\rangle, |10\rangle, |11\rangle\}$ :

$$\hat{\rho}'_{SS'}^{(2)} = \frac{1}{2} \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \quad (2.110)$$

This is not a positive semi-definite matrix, and hence not a valid density matrix. This matrix has a block diagonal form, with one of the blocks being like the sigma-x Pauli matrix, which is not a positive matrix. The problematic eigenvalue is  $-1/2$ , with eigenvector  $|\psi\rangle = \frac{1}{\sqrt{2}}(|01\rangle - |10\rangle)_{SS'}$ .

### General mathematical form of a CPTP map

Consider an auxiliary system  $R$  with the same dimension  $d$  as the system  $S$ . Let  $\{|i\rangle\}_{i=1}^d$  be an orthonormal basis. We define the maximally entangled state (unnormalized) on  $\mathcal{H}_R \otimes \mathcal{H}_S$ :

$$|\Gamma\rangle = \sum_{i=1}^d |i\rangle_R \otimes |i\rangle_S$$

Let us define:

$$C_\Phi \equiv (\mathcal{I}_R \otimes \Phi)[| \Gamma \rangle \langle \Gamma |] = \sum_{i,j} |i\rangle \langle j|_R \otimes \Phi[|i\rangle \langle j|_S]$$

$C_\Phi$  is called the Choi matrix corresponding to the map  $\Phi$ . Since  $\Phi$  is CPTP and  $| \Gamma \rangle \langle \Gamma |$  is a positive semi-definite operator,  $C_\Phi$  is a positive semi-definite operator. Hence,  $C_\Phi$  admits a spectral decomposition:

$$C_\Phi = \sum_k \lambda_k |v_k\rangle \langle v_k|$$

where  $\lambda_k \geq 0$  are the eigenvalues and  $|v_k\rangle \in \mathcal{H}_R \otimes \mathcal{H}_S$  are the orthonormal eigenvectors.

We can always find an operator  $\hat{A}_k \in \mathcal{L}(\mathcal{H}_S)$  for every vector  $|v_k\rangle$ , such that we have:

$$\sqrt{\lambda_k} |v_k\rangle = (\mathcal{I}_R \otimes \hat{A}_k) | \Gamma \rangle = \sum_i |i\rangle_R \otimes \hat{A}_k |i\rangle_S$$

Substituting this back into the spectral decomposition of the Choi matrix, we get:

$$C_\Phi = \sum_k (\mathcal{I}_R \otimes \hat{A}_k) | \Gamma \rangle \langle \Gamma | (\mathcal{I}_R \otimes \hat{A}_k^\dagger)$$

For any system state  $\hat{\rho} \equiv \sum_{i,j} \rho_{ij} |i\rangle \langle j|$ , we use the identity  $\hat{\rho} = \text{Tr}_R[(\hat{\rho}^T \otimes \mathcal{I}_S) | \Gamma \rangle \langle \Gamma |]$ . We can prove this as following:

$$\text{Tr}_R[(\hat{\rho}^T \otimes \mathcal{I}_S) | \Gamma \rangle \langle \Gamma |] = \sum_{i,j,p,q} \text{Tr}_R[\rho_{pq} |q\rangle \langle p|_i \langle j| \otimes |i\rangle \langle j|] \quad (2.111)$$

$$= \sum_{i,j,p,q} \rho_{pq} \langle p|i\rangle \langle j|q\rangle |i\rangle \langle j| \quad (2.112)$$

$$= \sum_{i,j} \rho_{ij} |i\rangle \langle j| = \hat{\rho} \quad (2.113)$$

Then, we have:

$$\Phi[\hat{\rho}] = \text{Tr}_R[(\mathcal{I} \otimes \Phi)(\hat{\rho}^T \otimes \mathcal{I}_S) | \Gamma \rangle \langle \Gamma |] \quad (2.114)$$

$$= \text{Tr}_R[(\hat{\rho}^T \otimes \mathcal{I}_S)(\mathcal{I} \otimes \Phi)[|I\rangle\langle I|]] \quad (2.115)$$

$$= \text{Tr}_R[(\hat{\rho}^T \otimes \mathcal{I}_S)C_\Phi] \quad (2.116)$$

$$= \text{Tr}_R \left[ (\hat{\rho}^T \otimes \mathcal{I}_S) \sum_k (\mathcal{I}_R \otimes \hat{A}_k) |I\rangle\langle I| (\mathcal{I}_R \otimes \hat{A}_k^\dagger) \right] \quad (2.117)$$

$$= \sum_k \hat{A}_k \left( \text{Tr}_R[(\hat{\rho}^T \otimes \mathcal{I}_S) |I\rangle\langle I|] \right) \hat{A}_k^\dagger \quad (2.118)$$

$$= \sum_k \hat{A}_k \hat{\rho} \hat{A}_k^\dagger \quad (2.119)$$

Finally, from the TP condition, we have:

$$\text{Tr} \left[ \sum_k \hat{A}_k \hat{\rho} \hat{A}_k^\dagger \right] = \text{Tr} \left[ \hat{\rho} \sum_k \hat{A}_k^\dagger \hat{A}_k \right] = \text{Tr}[\hat{\rho}]$$

Since this must hold for all  $\hat{\rho}$ , we must have:

$$\sum_k \hat{A}_k^\dagger \hat{A}_k = I$$

$\hat{A}_k$  are known as the Kraus operators. The representation  $\Phi[\hat{\rho}] = \sum_k \hat{A}_k \hat{\rho} \hat{A}_k^\dagger$  is known as the Kraus representation of the CPTP map  $\Phi$ .

## Global Unitary picture for a CPTP map

Can any CPTP map be equivalently thought of as arising from a global unitary evolution on a larger Hilbert space that includes an auxiliary environment system? The answer is yes. To see this equivalence, consider the initial SE state to be  $\hat{\rho}_{SE} = \hat{\rho}_S \otimes |0\rangle_E \langle 0|$ , where  $|0\rangle_E$  is some fixed pure state of the environment. Let the global SE unitary evolution be given as  $\hat{U}_{SE}$ . Then, we can define

$$\hat{U}_{SE} |0\rangle_E \equiv \sum_k \hat{A}_k \otimes |k\rangle_E. \quad (2.120)$$

Here,  $\hat{A}_k$  are operators acting on the system Hilbert space and  $\{|k\rangle_E\}$  is an orthonormal basis for the environment Hilbert space. To see that the above transformation is indeed unitary, for two orthogonal system states  $|\psi_1\rangle_S$  and  $|\psi_2\rangle_S$ , we need to show that  $\hat{U}_{SE}|\psi_1\rangle_S \otimes |0\rangle_E$  is orthogonal to  $\hat{U}_{SE}|\psi_2\rangle_S \otimes |0\rangle_E$ . We show this as following:

$$\langle \psi_1 |_S \otimes \langle 0 |_E \hat{U}_{SE}^\dagger \hat{U}_{SE} |\psi_2\rangle_S \otimes |0\rangle_E = \sum_{k,k'} \langle \psi_1 |_S \hat{A}_k^\dagger \hat{A}_{k'} |\psi_2\rangle_S \otimes \langle k |_E \langle k' |_E, \quad (2.121)$$

$$= \sum_k \langle \psi_1 |_S \hat{A}_k^\dagger \hat{A}_k |\psi_2\rangle_S, \quad (2.122)$$

$$= \langle \psi_1 |_S \left( \sum_k \hat{A}_k^\dagger \hat{A}_k \right) |\psi_2\rangle_S, \quad (2.123)$$

$$= \langle \psi_1 |_S \mathcal{I}_S |\psi_2\rangle_S = 0. \quad (2.124)$$

Next, we note that Eq. (2.120) does not define the action of  $\hat{U}_{SE}$  on states of the form  $|\psi\rangle_S \otimes |k\rangle_E$  for  $k \neq 0$ . But the action of  $\hat{U}_{SE}$  on such states can be defined consistently in a non-unique manner to make  $\hat{U}_{SE}$  a full unitary operator on the joint SE Hilbert space. But this is irrelevant to the current discussion.

We now evaluate the action of  $\hat{U}_{SE}$  on the initial SE state  $\hat{\rho}_{SE} = \hat{\rho}_S \otimes |0\rangle_E \langle 0|$  as following:

$$\text{Tr}_E \{ \hat{U}_{SE} \hat{\rho}_{SE} \hat{U}_{SE}^\dagger \} = \text{Tr}_E \{ \hat{U}_{SE} (\hat{\rho}_S \otimes |0\rangle_E \langle 0|) \hat{U}_{SE}^\dagger \}, \quad (2.125)$$

$$= \sum_{k,k'} \text{Tr}_E \{ (\hat{A}_k \hat{\rho}_S \hat{A}_{k'}^\dagger) \otimes (|k\rangle_E \langle k'|) \}, \quad (2.126)$$

$$= \sum_k \hat{A}_k \hat{\rho}_S \hat{A}_k^\dagger \quad (2.127)$$

$$= \Phi[\hat{\rho}_S]. \quad (2.128)$$

This equivalence is called the Stinespring dilation theorem.

### 2.3.2 Memoryless Open Quantum System Maps

Consider a physical open quantum system map  $\Phi_t$ . Suppose that for all  $t_2 \geq t_1 \geq 0$ , there exists a CPTP map  $\Lambda_{t_2, t_1}$  such that

$$\Phi_{t_2} = \Lambda_{t_2, t_1} \circ \Phi_{t_1}. \quad (2.129)$$

Then, the map  $\Phi_t$  is said to be CP-divisible. We will define memoryless (or Markovian) open quantum system maps as those that are CP-divisible.

This definition is physically motivated because, since  $\Lambda_{t_2, t_1}$  is a CPTP map, using the Stinespring dilation theorem, we can think of the evolution from *any times*  $t_1$  to  $t_2$  as arising from a global unitary evolution on a larger Hilbert space, where the initial state is  $\hat{\rho}(t_1) \otimes \hat{\rho}_E$  for some fixed environment state  $\hat{\rho}_E$ . Hence, for all practical purposes,  $\Phi_t$  is indistinguishable from a dynamics where the system is interacting with a fresh environment at each moment in time, where the latter is a memoryless process.

We note that using CP-divisibility as the definition of Markovianity is applicable only because we are not allowing for probing of the system at intermediate times. If we allow for such probing at intermediate times, then it has been shown that CP divisible dynamics can also show memory effects [95]. But for the purpose of this thesis, we will not allow for such probing at intermediate times, and hence we will use CP-divisibility as the definition of Markovianity.

#### Distinguishability of quantum states under CPTP maps

Since unitary evolution is a reversible process, it cannot lead to phenomena like equilibration or thermalization. Certain CPTP maps, though, can lead to these phenomena. In other words, quantum states tend to become less distinguishable under the action of *some* CPTP maps. This section will formalize this intuition. This can be quantified using the

trace distance between two quantum states, which is a measure of their distinguishability.

The trace distance between two states is defined as [96]

$$D(\hat{\rho}_1, \hat{\rho}_2) = \frac{1}{2} \|\hat{\rho}_1 - \hat{\rho}_2\|_1, \quad (2.130)$$

where the trace norm is defined as  $\|\hat{X}\|_1 \equiv \text{Tr} \sqrt{\hat{X}^\dagger \hat{X}}$ . Then, we state and prove the following proposition.

**Proposition 2.** *Let  $\hat{\rho}$  and  $\hat{\sigma}$  be density operators on a Hilbert space  $\mathcal{H}$ , and let  $\Phi : \mathcal{L}(\mathcal{H}) \rightarrow \mathcal{L}(\mathcal{H}')$  be a CPTP map. Then the trace distance  $D(\hat{\rho}, \hat{\sigma}) = \frac{1}{2} \|\hat{\rho} - \hat{\sigma}\|_1$  satisfies:*

$$D(\Phi[\hat{\rho}], \Phi[\hat{\sigma}]) \leq D(\hat{\rho}, \hat{\sigma}) \quad (2.131)$$

*Proof.* Let  $\hat{X} \equiv \hat{\rho} - \hat{\sigma}$ . Since  $\hat{X}$  is Hermitian, we can decompose it into its positive and negative parts:

$$\hat{X} = \hat{X}_+ - \hat{X}_- \quad (2.132)$$

where  $\hat{X}_+, \hat{X}_- \geq 0$  are positive semi-definite operators with orthogonal supports. The trace norm is given by:

$$\|\hat{X}\|_1 = \text{Tr}(\hat{X}_+) + \text{Tr}(\hat{X}_-) \quad (2.133)$$

Using the linearity of the map  $\Phi$ , we have,

$$\Phi[\hat{\rho}] - \Phi[\hat{\sigma}] = \Phi[\hat{X}] = \Phi[\hat{X}_+] - \Phi[\hat{X}_-] \quad (2.134)$$

We now consider the trace norm of the difference of the transformed states:

$$\|\Phi[\hat{\rho}] - \Phi[\hat{\sigma}]\|_1 = \|\Phi[\hat{X}_+] - \Phi[\hat{X}_-]\|_1 \quad (2.135)$$

Applying the triangle inequality for the trace norm ( $\|A + B\|_1 \leq \|A\|_1 + \|B\|_1$ ), we get,

$$\|\Phi[\hat{X}_+] - \Phi[\hat{X}_-]\|_1 \leq \|\Phi[\hat{X}_+]\|_1 + \|\Phi[\hat{X}_-]\|_1 \quad (2.136)$$

$$= \|\Phi[\hat{X}_+]\|_1 + \|\Phi[\hat{X}_-]\|_1 \quad (2.137)$$

$$= \text{Tr}(\hat{X}_+) + \text{Tr}(\hat{X}_-) \quad (2.138)$$

$$= \|\hat{X}\|_1 \quad (2.139)$$

Here, we used the fact that since  $\hat{X}_\pm \geq 0$ , we have  $\Phi[\hat{X}_\pm] \geq 0$  from the CP condition of  $\Phi$ . This means that  $\|\Phi[\hat{X}_\pm]\|_1 = \text{Tr}(\Phi[\hat{X}_\pm])$ . Similarly, from the TP condition of  $\Phi$ , we used  $\text{Tr}(\Phi[\hat{X}_\pm]) = \text{Tr}(\hat{X}_\pm)$ .

From Eq. (2.139), we therefore have,

$$\|\Phi[\hat{X}]\|_1 \leq \|\hat{X}\|_1, \quad (2.140)$$

$$\implies \|\Phi[\hat{\rho}] - \Phi[\hat{\sigma}]\|_1 \leq \|\hat{\rho} - \hat{\sigma}\|_1, \quad (2.141)$$

$$D(\Phi[\hat{\rho}], \Phi[\hat{\sigma}]) \leq D(\hat{\rho}, \hat{\sigma}). \quad (2.142)$$

This completes the proof of Proposition 2.  $\square$

For CP-divisible dynamics, the intermediate map  $\Lambda_{t_2, t_1}$  is CPTP for all  $t_2 \geq t_1 \geq 0$ . Therefore, from Proposition 2, we have that for CP-divisible dynamics, the trace distance between any two states must monotonically decrease over time.

### 2.3.3 The BLP measure of non-Markovianity

We have defined memoryless open quantum system maps as those that are CP-divisible. By extension, let us now define non-Markovian open quantum system maps as those that are not CP-divisible. The trace distance between two quantum states for non-Markovian dynamics hence can increase at certain times. This increase in trace distance can be

physically interpreted as a backflow of information from the environment to the system, which is a hallmark of non-Markovian dynamics.

The Breuer-Laine-Piilo (BLP) measure of non-Markovianity tries to quantify this backflow of information [50, 97]. Assuming that the dynamics of the open quantum system is described by a completely positive trace preserving (CPTP) map  $\Phi_t$ , the degree of non-Markovianity of dynamics is defined by [97]

$$\mathcal{N}(\Phi) = \max_{\hat{\rho}_{1,2}(0)} \int_{\sigma>0} dt \sigma(t, \hat{\rho}_{1,2}(0)), \quad (2.143)$$

where  $\sigma(t, \hat{\rho}_{1,2}(0)) = \frac{d}{dt} D[\Phi_t(\hat{\rho}_1(0)), \Phi_t(\hat{\rho}_2(0))]$ . A non-zero value of  $\mathcal{N}(\Phi)$  indicates backflow of information from the environment to the system. Since the measure  $\mathcal{N}(\Phi)$  involves a maximization over all pairs of initial states, it quantifies the maximum possible information backflow.

We note that for linear maps, it has been shown that the BLP measure is optimized by orthogonal states [98]. For a qubit system, this implies that the optimal states are antipodal, which greatly simplifies the evaluation of the BLP measure. Here, we reproduce the necessary proof from [98].

**Proposition 3.** *Assume  $\mathcal{N}(\Phi) > 0$ . Let  $\hat{\rho}_1(0)$  and  $\hat{\rho}_2(0)$  be a pair of initial states that attains the maximum in the definition of the BLP measure  $\mathcal{N}(\Phi)$  in Eq. (2.143). Then,*

$$D(\hat{\rho}_1(0), \hat{\rho}_2(0)) = 1. \quad (2.144)$$

*For qubit systems, this implies that these states are antipodal.*

*Proof.* We will prove this result via contradiction. Assume that this optimal pair is not orthogonal. This means  $D(\hat{\rho}_1(0), \hat{\rho}_2(0)) < 1$ .

As we did in Proposition 2, let  $\hat{X} \equiv \hat{\rho}_1(0) - \hat{\rho}_2(0)$ . Since  $\hat{X}$  is Hermitian, we can decompose

it into its positive and negative parts:

$$\hat{X} = \hat{X}_+ - \hat{X}_- \quad (2.145)$$

where  $\hat{X}_+, \hat{X}_- \geq 0$  are positive semi-definite operators with orthogonal supports. Since  $\text{Tr}(\hat{X}) = 0$ , we have

$$D(\hat{\rho}_1(0), \hat{\rho}_2(0)) = \text{Tr}(\hat{X}_+) = \text{Tr}(\hat{X}_-). \quad (2.146)$$

Define

$$\hat{\rho}'_1(0) = \frac{\hat{X}_+}{D(\hat{\rho}_1(0), \hat{\rho}_2(0))}, \quad \hat{\rho}'_2(0) = \frac{\hat{X}_-}{D(\hat{\rho}_1(0), \hat{\rho}_2(0))}. \quad (2.147)$$

$\hat{\rho}'_i(0)$  are quantum states. We have:

$$\hat{\rho}'_1(0) - \hat{\rho}'_2(0) = \frac{\hat{\rho}_1(0) - \hat{\rho}_2(0)}{D(\hat{\rho}_1(0), \hat{\rho}_2(0))}. \quad (2.148)$$

Hence, by linearity,

$$\Phi_t(\hat{\rho}'_1(0)) - \Phi_t(\hat{\rho}'_2(0)) = \frac{1}{D(\hat{\rho}_1(0), \hat{\rho}_2(0))} [\Phi_t(\hat{\rho}_1(0)) - \Phi_t(\hat{\rho}_2(0))]. \quad (2.149)$$

This directly gives

$$\int_{\sigma>0} dt \sigma(t, \hat{\rho}'_{1,2}(0)) = \frac{1}{D(\hat{\rho}_1(0), \hat{\rho}_2(0))} \int_{\sigma>0} dt \sigma(t, \hat{\rho}_{1,2}(0)). \quad (2.150)$$

Since the assumed trace distance is less than one, the primed pair gives a larger value of the BLP measure in Eq. (2.143) than the supposedly optimal pair. This is a contradiction. Therefore, the trace distance between the optimal pair must equal one. This concludes the proof of Proposition 3.  $\square$

This concludes our background discussion on the non-Markovianity of open quantum system dynamics relevant for the results presented in this thesis.

## 2.4 Numerically exact approaches to Open Quantum System Dynamics

Several numerically exact techniques to solve for the open system dynamics are available, like Hierarchical Equations of Motion (HEOM) [99] and Tensor Networks [100]. These techniques have played an important role in the study of open quantum systems beyond the weak-coupling approximations. Though, the computational cost of using these techniques does not scale well with system size and SE coupling strength. This serves as one of the motivations for developing perturbative techniques like the TCL formalism.

In the present thesis, we will be using the HEOM technique to benchmark our TCL2 and TCL4 results. The HEOM technique is a non-perturbative approach for solving the dynamics of an open quantum system based on Feynman-Vernon influence functional formalism [99, 101–103]. For introduction to the analogous imaginary-time Feynman–Vernon path-integral formulation, see Sec. 2.5.2.

In this thesis, we have used the HEOM solver provided in the Qutip package [104, 105] for our calculations for Ohmic spectral density with Drude cutoff (Eq. (2.89)). The numerical implementation of HEOM comes with some precision parameters that need to be tuned to achieve the desired accuracy. For the present consideration, these include

1. the number of Matsubara terms retained in the expression of the two-point correlation function in Eq. (2.90) and Eq. (2.91). A higher number of Matsubara terms need to be retained in the low-temperature limit [103];
2. the number of hierarchical equations retained: The HEOM technique involves expressing the open system dynamics in terms of an infinite hierarchy of differential

equations for the so-called auxiliary density operators, where the zeroth order term corresponds to the exact time-dependent state of the system [102]. Truncating these coupled differential equations at some order provides an approximation to the exact dynamics, providing a finite system of coupled differential equations that can in principle be solved numerically, given the initial conditions. Although, the computational cost of solving these equations increases with the order of truncation.

## 2.5 Mean-force Gibbs State

### 2.5.1 Caldeira–Leggett model

For this section, we will consider the more general Caldeira–Leggett (CL) model for the open quantum system [106], which shares similarities with the SBM, such as coupling to non-interacting bosonic modes, while at the same time having an arbitrary-dimensional quantum system (like a qutrit or a continuous-variable quantum system) rather than a two-level system as in the case of the SBM. Under the CL model, the system, with generic free Hamiltonian  $\hat{H}_S$ , interacts with a large number of harmonic oscillators that are uncoupled from each other. The full SE Hamiltonian is hence given by

$$\hat{H}_{\text{SE}} = \hat{H}_S + \hat{H}_I, \quad (2.151)$$

$$\hat{H}_I = \sum_k \left[ \frac{\hat{p}_k^2}{2m_k} + \frac{1}{2} m_k \omega_k^2 (\hat{q}_k - \alpha_k \hat{A})^2 \right], \quad (2.152)$$

where  $\hat{A}$  is a generic system operator through which the system couples to the environment (which from now onwards we will refer to as ‘system coupling-operator’) and

$$\alpha_k \equiv \frac{c_k}{m_k \omega_k^2}, \quad (2.153)$$

where  $m_k$  and  $\omega_k$  are the mass and frequency of the  $k$ th harmonic oscillator and  $c_k$  is the corresponding SE coupling strength. For a continuous variable (CV) system, typically we have  $\hat{A} = \hat{q}$ , where  $\hat{q}$  is the position operator of the system [2, 4, 66]. We note that in a certain limit, a CL model describing the dissipative dynamics of a double-well system, which is a continuous-variable system, can be reduced to an SBM [54].

## 2.5.2 Path integral approach to Mean Force Gibbs State

The MFGS (Eq. (1.1)) can be calculated using the Feynman path integral [107] in the basis of the operators  $\hat{A}$  and  $\hat{q}_k$  by evolving the system and the environment in the ‘imaginary time’ by an amount  $\beta$  and then tracing over the environment degrees of freedom. [4, 53]

Note a subtlety that arises when the system coupling-operator  $\hat{A}$  has degeneracy, and hence each of its eigenstates is not uniquely labelled by an eigenvalue. This would mean that the path integral in the basis of  $\hat{A}$  cannot distinguish between different paths that the system can take within the degenerate subspace of  $\hat{A}$ .

To fix this problem, let us introduce a non-degenerate operator  $\hat{\phi}$  commuting with  $\hat{A}$ . The final result will not depend upon the particular choice of  $\hat{\phi}$ . Let  $\rho(a, b)$  be the  $(a, b)$ -th element of  $\hat{\rho}$  in the eigenbasis of  $\hat{\phi}$ , corresponding to its eigenvalues  $a$  and  $b$ .

Let a generic imaginary time path be denoted as  $\{A(t), \phi(t), q_k(t)\}$ , where  $A(t) \in \{A_i\}$ ,  $\phi(t) \in \{\phi_i\}$ , and  $q_k(t) \in \{q_{ki}\}$ , where  $\{A_i\}$ ,  $\{\phi_i\}$  and  $\{q_{ki}\}$  are the sets of eigenvalues of operators  $\hat{A}$ ,  $\hat{\phi}$  and  $\hat{q}_k$ , respectively. We emphasize here that  $A(t)$  denotes a path that the system can take in the path integral and should not be confused to mean that the system coupling-operator,  $\hat{A}$ , has a time dependence. In fact,  $\hat{A}$  has been assumed to be time-independent throughout this paper.

Now, let  $S_S[A(t), \phi(t)]$  and  $S_I[A(t), q_k(t)]$  represent the imaginary time action corresponding to  $\hat{H}_S$  and  $\hat{H}_I$ , respectively. Note how  $S_I$  does not depend upon  $\phi(t)$  while  $S_S$  does. This is because while  $\hat{H}_S$  is an arbitrary system operator,  $\hat{H}_I$  has system dependence

only through the operator  $\hat{A}$ , and hence the corresponding action,  $S_I$ , cannot distinguish within the degenerate subspace of  $\hat{A}$ , which removes the  $\phi(t)$  dependence.

Also note that the paths  $A(t)$  and  $\phi(t)$  are not independent of each other. That is,  $A(t)$  and  $\phi(t)$  denote some eigenvalues of the operators  $\hat{A}$  and  $\hat{\phi}$ , respectively, such that one can find a common eigenvector  $|v(t)\rangle \equiv |A(t), \phi(t)\rangle$  such that  $\hat{A}|v(t)\rangle = A(t)|v(t)\rangle$  and  $\hat{\phi}|v(t)\rangle = \phi(t)|v(t)\rangle$ . But we can always treat  $A(t)$  and  $\phi(t)$  as independent of each other if we assume that the action  $S_S[A(t), \phi(t)]$  is constructed in such a manner that, given some  $A(t)$ , it rules out all unphysical possibilities for the path  $\phi(t)$  by assigning the corresponding action an infinite weight. For all the arguments in this paper, we *don't* need to go into any further details on how to construct such a functional  $S_S[A(t), \phi(t)]$ .

The full SE path integral is given as

$$\begin{aligned} \rho(a, b, a_k, b_k) = & \tilde{Z}^{-1} \left( \prod_k \int_{a_k}^{b_k} \mathcal{D}q_k(t) \right) \int_{\tilde{a}}^{\tilde{b}} \mathcal{D}A(t) \\ & \times \int_a^b \mathcal{D}\phi(t) e^{-S_S[A(t), \phi(t)] - S_I[A(t), q_k(t)]}. \end{aligned} \quad (2.154)$$

Here  $\tilde{Z}$  is the overall normalization factor and  $a, b, a_k, b_k, \tilde{a}$ , and  $\tilde{b}$  correspond to  $\phi(0)$ ,  $\phi(\beta)$ ,  $q_k(0)$ ,  $q_k(\beta)$ ,  $A(0)$ , and  $A(\beta)$ , respectively. Moreover,  $\int_x^y \mathcal{D}z(t)$  denotes the path integral over all paths  $z(t)$  such that  $z(0) = x$  and  $z(\beta) = y$ .

Tracing over the environment means that we restrict the paths  $q_k(t)$  to be closed, i.e.,  $q_k(0) = q_k(\beta)$ , and then integrate over all such paths. This will now give us the MFGS as

$$\rho(a, b) = \left( \prod_k \int_{-\infty}^{\infty} da_k \right) \rho(a, b, a_k, a_k) \quad (2.155)$$

$$= \tilde{Z}^{-1} \int_{\tilde{a}}^{\tilde{b}} \mathcal{D}A(t) \int_a^b \mathcal{D}\phi(t) e^{-S_S[A(t), \phi(t)]} I[A(t)]. \quad (2.156)$$

Here  $I[A(t)] \equiv \prod_k I_k[A(t)]$  is called the influence functional [4, 53], where  $I_k[A(t)]$  en-

capsulates the effect of the  $k$ th environment particle only and is defined as

$$I_k[A(t)] = \int_{-\infty}^{\infty} dx \int_x^x \mathcal{D}q_k(t) e^{-S_k[q_k(t), A(t)]}. \quad (2.157)$$

Here the action,  $S_k$ , can be derived as [4]

$$S_k[q_k(t), A(t)] \equiv \int_0^\beta dt \left\{ \frac{m_k}{2} \dot{q}_k(t)^2 + \frac{m_k \omega_k^2}{2} (q_k(t) - \alpha_k A(t))^2 \right\}. \quad (2.158)$$

The explicit expression for  $I[A(t)]$  for CL model [4,53] can be used to derive the CL-USC result. [81, 108] But here, since we need to eventually generalize this result beyond the CL model, we will derive the expression for the USC-MFGS without explicitly evaluating  $I[A(t)]$  for any specific model. The rest of the derivation is presented in Chapter 5.

## Chapter 3

# Time-Convolutionless Master Equation at Fourth Order

This chapter involves the derivation of the TCL4-ME for a SBM and the calculation of the second order corrections to the SS populations and coherences. The SS corrections are compared with the corresponding MFGS results [22].

This chapter is structured as follows. Sec. 3.1 and Sec. 3.2 contain the calculation of second order SS coherences and populations, which requires us to evaluate the TCL2 and TCL4 generator, respectively. Sec. 3.3 discusses the assumptions we take for the spectral density and the limitations of our results. Sec. 3.4 contains the technical details of the calculations. The actual calculations can be found in the Supplementary Material [52].

### 3.1 Second order steady-state coherences

In this section, for completeness, we provide the derivation for the second order SS coherences for a SBM and its equivalence with the corresponding MFGS coherences, which only requires the TCL2 generator and has previously been derived elsewhere [1, 8–10].

### 3.1.1 Properties of a generic open quantum system

In Sec. 3.4.1, we show that, given that  $\hat{A}$  is the operator through which the system is coupled to the environment (see Eq. (2.58)), for a system operator  $\hat{O}_1$  defined such that

$$[\hat{O}_1, \hat{A}] \equiv 0, \quad (3.1)$$

then even at arbitrarily strong SE coupling, we have

$$\frac{d}{dt} \langle \hat{O}_1 \rangle_{\hat{\rho}_S(t)} = \text{Tr} \{ -i[\hat{O}_1, \hat{H}_S] \hat{\rho}_S(t) \}. \quad (3.2)$$

That is, the expectation value of  $\hat{O}_1$  is evolved by only the free Hamiltonian. Then, in the large time limit, we have

$$\frac{d}{dt} \langle \hat{O}_1 \rangle_{\hat{\rho}_S(t)} = 0 = \lim_{t \rightarrow \infty} \text{Tr} \{ -i[\hat{O}_1, \hat{H}_S] \hat{\rho}_S(t) \}. \quad (3.3)$$

Defining

$$\hat{O}_2 \equiv [\hat{O}_1, \hat{H}_S], \quad (3.4)$$

we then have that,

$$\langle \hat{O}_2 \rangle_{SS} = 0. \quad (3.5)$$

Here,  $\langle \hat{O} \rangle_{SS}$  denotes the exact SS expectation value of the operator  $\hat{O}$ .

As we prove in Sec. 3.4.1, we note that this is a non-perturbative result which holds for arbitrary value of  $\lambda$  and hence holds not just for TCL2n-ME for arbitrary  $n$ , but also in intermediate and strong SE coupling regime where TCL fails. This result is also valid for a generic  $d$ -dimensional system.

This result is relevant in the present discussion because choosing  $\hat{O}_1 = \hat{A}$ , for the SBM, we get (from Eq. (2.72), Eq. (2.74) and Eq. (3.4)) that

$$\hat{O}_2 = [\hat{A}, \hat{H}_S] \propto \hat{\sigma}_2. \quad (3.6)$$

This means that, to all orders in TCL, we have

$$\langle \hat{\sigma}_2 \rangle_{SS}^{(2n)} = v_2^{(2n)} = 0, \quad (3.7)$$

$$\implies v_2^{(2)} = 0. \quad (3.8)$$

Here, we use the Bloch vector representation for the SBM, as defined in Sec. 2.2.3.

As a side note, we also prove in Sec. 3.4.1 that the corresponding MFGS expectation value for  $\hat{O}_2$  (Eq. (3.5)) is also zero at arbitrary SE coupling.

### 3.1.2 General properties of TCL generator

We can use the above result to deduce certain general properties of the TCL $2n$  generator matrices. Technically, the TCL $2n$  generator matrix for SBM has 16 elements (see Sec. 2.2.3). However, we will now show that only 8 of these elements are independent.

General properties of the TCL $2n$  generator matrices include  $F_{0k}^{(2n)} = 0$  for all  $k$  due to trace preservation condition ( $\dot{v}_0(t) = 0$ ). This eliminates 4 elements.

Next, choosing  $\hat{O}_1 = \hat{A}$  in Eq. (3.1), we have Eq. (3.2) transform as,

$$\frac{d}{dt} \langle \hat{A} \rangle_{\hat{\rho}_S(t)} = \text{Tr} \{ -i [\hat{A}, \hat{H}_S] \hat{\rho}_S(t) \}. \quad (3.9)$$

This means that the expectation value of  $\hat{A}$  is only evolved by TCL0. Hence, for  $n \geq 1$ ,

we have

$$\text{Tr} \{ \hat{A} \mathcal{F}^{(2n)}(t) [\hat{\rho}] \} = 0 \quad \forall \hat{\rho}, \quad (3.10)$$

$$\implies \text{Tr} \{ \hat{A} \mathcal{F}^{(2n)}(t) [\hat{\sigma}_k] \} = 0 \text{ replacing } \hat{\rho} \rightarrow \hat{\sigma}_k, \quad (3.11)$$

$$\implies \text{Tr} \{ (a_3 \hat{\sigma}_3 - a_1 \hat{\sigma}_1) \mathcal{F}^{(2n)}(t) [\hat{\sigma}_k] \} = 0, \quad \text{using Eq. (2.74)} \quad (3.12)$$

$$\implies a_3 F_{3k}^{(2n)}(t) = a_1 F_{1k}^{(2n)}(t), \quad \text{using Eq. (2.102)}. \quad (3.13)$$

This gives us 4 more constraints on the TCL2n generator matrix elements. This finally leaves us with only 8 independent elements in the TCL2n generator matrix for SBM. This will greatly simplify the calculations for higher order TCL-ME for SBM.

### 3.1.3 TCL2 steady-state coherences

Next, to calculate the only non-zero second order correction to the SS coherences,  $v_1^{(2)}$ , we extract the  $O(\lambda^2)$  term from perturbative expression for the TCL SS (Eq. (2.67)) as,

$$F^{(0)} \vec{v}^{(2)} + F^{(2)} \vec{v}^{(0)} = 0. \quad (3.14)$$

The zeroth order terms in this equation are given as

$$F^{(0)} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & -\Omega & 0 \\ 0 & \Omega & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad (3.15)$$

$$\vec{v}^{(0)} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ v_3^{(0)} \end{pmatrix}. \quad (3.16)$$

The 3rd row of the matrix on the LHS of Eq. (3.14) then gives us,

$$v_1^{(2)} = -\frac{F_{20}^{(2)} + v_3^{(0)} F_{23}^{(2)}}{\Omega}. \quad (3.17)$$

The matrix elements for the TCL2 generator ( $F_{20}^{(2)}$  and  $F_{23}^{(2)}$ ) can be evaluated for an arbitrary open quantum system (see [3, 94]). The details of the calculations and solutions of all the elements of the TCL2 generator are given in Sec. 3.4.2. For the present case, for example, we have

$$F_{20}^{(2)} = -4a_1 a_3 \lim_{t \rightarrow \infty} \int_0^t dt_1 \eta(t - t_1) (\cos((t - t_1)\Omega) - 1), \quad (3.18)$$

$$F_{23}^{(2)} = -4a_1 a_3 \lim_{t \rightarrow \infty} \int_0^t dt_1 v(t - t_1) \sin((t - t_1)\Omega). \quad (3.19)$$

Here,  $v(t)$  and  $\eta(t)$  are the real and imaginary part of the environment's two point correlation function, defined as,

$$\eta(t) \equiv \Im\{\langle \hat{B}, \hat{B}(-t) \rangle\}, \quad (3.20)$$

$$v(t) \equiv \Re\{\langle \hat{B}, \hat{B}(-t) \rangle\}, \quad (3.21)$$

and in terms of the spectral density, can be evaluated to be (following Eq. (2.86)):

$$\eta(t) = -\int_0^\infty d\omega J(\omega) \sin(t\omega), \quad (3.22)$$

$$v(t) = \int_0^\infty d\omega f(\omega) \cos(t\omega), \quad (3.23)$$

where, we have defined

$$f(\omega) \equiv J(\omega) \coth(\beta\omega/2). \quad (3.24)$$

For an arbitrary spectral density,  $J(\omega)$ , in Eq. (3.18) and Eq. (3.19), we first do the  $t_1$  integral analytically, and then take the large  $t$  limit (see the supplementary material [52]

for detailed calculations). In this case, the result can be evaluated as,

$$F_{20}^{(2)} = 4a_1a_3\Omega^2 \int_0^\infty d\omega \frac{J(\omega)}{\omega^3 - \omega\Omega^2}, \quad (3.25)$$

$$F_{23}^{(2)} = 4a_1a_3\Omega \int_0^\infty d\omega \frac{f(\omega)}{\omega^2 - \Omega^2}, \quad (3.26)$$

which, using Eq. (3.17), yields

$$v_1^{(2)} = 4a_1a_3 \int_0^\infty d\omega \frac{J(\omega) \left( \omega \coth\left(\frac{\beta\omega}{2}\right) \tanh\left(\frac{\beta\Omega}{2}\right) - \Omega \right)}{\omega^3 - \omega\Omega^2}. \quad (3.27)$$

This matches with the corresponding MFGS expression [1, 8–10, 22]. It is also possible to verify that  $v_2^{(2)} = 0$  using similar calculations, consistent with the more general proof we have provided (see the Supplementary Material [52]).

## 3.2 Second order steady state population

We cannot use the  $O(\lambda^2)$  terms in the perturbative equation for the SS (Eq. (2.67)) to get the  $O(\lambda^2)$  correction to the populations ( $v_3^{(2)}$ ) because when we solve this  $O(\lambda^2)$  (Eq. (3.14)), the term of interest ( $v_3^{(2)}$ ) disappears from the expression. In fact, it is generically true that, in order to get the  $O(\lambda^{2n})$  correction to the populations, one needs to go to  $O(\lambda^{2n+2})$  ME [9]. In this case, the  $O(\lambda^4)$  terms in the perturbative equation for the SS (Eq. (2.67)) give us

$$F^{(0)}\vec{v}^{(4)} + F^{(2)}\vec{v}^{(2)} + F^{(4)}\vec{v}^{(0)} = 0. \quad (3.28)$$

From the 4th row of the matrix in the LHS of Eq. (3.28), we get

$$v_3^{(2)} = -\frac{F_{30}^{(4)} + v_3^{(0)}F_{33}^{(4)} + v_1^{(2)}F_{31}^{(2)}}{F_{33}^{(2)}}. \quad (3.29)$$

The expressions for  $F_{33}^{(2)}$  and  $F_{31}^{(2)}$  can be evaluated as in the last section. The expressions for the integrals for all the TCL2 matrix elements as well as their solutions are provided in Sec. 3.4.2.

To simplify the integrals for the TCL4 coefficients in Eq. (3.29), we assume single-valued, odd spectral densities that decay at least as  $1/\omega$  in the large- $\omega$  limit (see Sec. 3.3.1 for details). Then, the TCL4 coefficients can be written as [94, 109]

$$\begin{aligned}
F_{33}^{(4)} = \lim_{t \rightarrow \infty} 16a_1^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 & \\
& \left\{ a_3^2 \left[ \eta(t_1 - t_2) \eta(t - t_3) \left( \cos((t - t_2)\Omega) - \cos((t - t_1)\Omega) \right) \right. \right. \\
& \quad + \eta(t - t_2) \eta(t_1 - t_3) \left( \cos((t - t_2)\Omega) - \cos((t - t_1)\Omega) \right) \\
& \quad \left. \left. + \nu(t_1 - t_2) \nu(t - t_3) \left( \cos((t - t_3)\Omega) - \cos((t - t_2)\Omega) \right) \right] \right. \\
& \quad + a_1^2 \left[ \nu(t_1 - t_2) \nu(t - t_3) \sin((t - t_2)\Omega) \sin((t_1 - t_3)\Omega) \right. \\
& \quad \left. \left. + \nu(t - t_2) \nu(t_1 - t_3) \sin((t_1 - t_2)\Omega) \sin((t - t_3)\Omega) \right] \right\}, \quad (3.30)
\end{aligned}$$

$$\begin{aligned}
F_{30}^{(4)} = \lim_{t \rightarrow \infty} 8a_1^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 & \\
& \left\{ a_1^2 \left[ \eta(t_1 - t_2) \nu(t - t_3) \left( \sin((t + t_1 - t_2 - t_3)\Omega) - \sin((t - t_1 + t_2 - t_3)\Omega) \right) \right. \right. \\
& \quad + 2\eta(t_1 - t_3) \nu(t - t_2) \sin((t_1 - t_2)\Omega) \cos((t - t_3)\Omega) \\
& \quad \left. \left. - 2\eta(t - t_3) \nu(t_1 - t_2) \sin((t_2 - t_3)\Omega) \cos((t - t_1)\Omega) \right] \right. \\
& \quad + 2a_3^2 \left[ \eta(t_1 - t_3) \nu(t - t_2) \left( \sin((t - t_2)\Omega) - \sin((t - t_1)\Omega) \right) \right. \\
& \quad + \eta(t - t_3) \nu(t_1 - t_2) \left( \sin((t - t_2)\Omega) - \sin((t - t_3)\Omega) \right) \\
& \quad \left. \left. + \eta(t_1 - t_2) \nu(t - t_3) \left( \sin((t - t_2)\Omega) - \sin((t - t_1)\Omega) \right) \right] \right\}. \quad (3.31)
\end{aligned}$$

To calculate the TCL4 coefficients for a broad class of spectral density we are considering,

we must solve a five-dimensional integral as given in Eqs. (3.30) and (3.31). These integrals involve three time variables ( $t_1$ ,  $t_2$ , and  $t_3$ ) and two frequency variables ( $\omega_1$  and  $\omega_2$ , which are part of the functions  $\eta(t)$  and  $\nu(t)$ , as described in Eq. (3.22) and Eq. (3.23)). These time and frequency integrals are not separable because the time dependence in the integral expressions for  $\eta(t)$  and  $\nu(t)$  couples the time and frequency integrations. Since we do not assume a specific form for the  $J(\omega)$ , we keep the expressions for  $\eta(t)$  and  $\nu(t)$  explicit in terms of the frequency integrals and first evaluate the triple integral over the time variables, contained within the curly brackets in the following symbolic representation:

$$\lim_{t \rightarrow \infty} \int_0^\infty d\omega_2 \int_0^\infty d\omega_1 \left\{ \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 g(t, \omega_1, \omega_2, t_1, t_2, t_3) \right\} \quad (3.32)$$

Here, the function  $g(t, \omega_1, \omega_2, t_1, t_2, t_3)$  is a symbolic representative of the complicated TCL4 integrand, such as given in Eq. (3.30). The triple time integral is readily handled by a computer algebra system such as Mathematica. Following this, we carefully calculate the remaining double integral over the frequency variables in the large  $t$  limit, which can be symbolically represented as follows:

$$\lim_{t \rightarrow \infty} \int_0^\infty d\omega_2 \int_0^\infty d\omega_1 g'(t, \omega_1, \omega_2) \quad (3.33)$$

Fubini's theorem states that the order of integrals can be exchanged when the integrand is continuous and integrable (integral of its absolute value is convergent) [110], which may not be true in our case (Eq. (3.32) and Eq. (3.33)), for example, because of the presence of singularities. But we have numerically verified the validity of the interchange of the frequency and time integrals in Eq. (3.32) for the specific choice of Ohmic spectral density with Drude cutoff (see Sec. 4.3.1). We emphasize this because we did encounter a violation of Fubini's theorem while evaluating the remaining frequency integrals (Eq. (3.33)). See Sec. 3.4.4 for further discussions.

Given the complex nature of the analytical expressions for the matrix elements of  $F^{(4)}$ , they are not reproduced in their entirety within this thesis. Please see the accompanying supplementary materials for the full derivation and the final results in electronic form [52].

We note that a single universal Mathematica function was written to evaluate all the matrix coefficients of  $F^{(4)}$ . The final result generically looks like

$$F_{ij}^{(4)} = h_{ij} + \int_{-\infty}^{\infty} d\omega h'_{ij}(\omega) + \int_{-\infty}^{\infty} d\omega_2 \int_{-\infty}^{\infty} d\omega_1 h''_{ij}(\omega_1, \omega_2). \quad (3.34)$$

That is, the final expression can be written as a sum over a constant term ( $h_{ij}$ ) and a single and double frequency integral over functions  $h'_{ij}(\omega)$  and  $h''_{ij}(\omega_1, \omega_2)$ , respectively. We note that in the large time limit of the integrand in Eq. (3.33), the terms that have time dependence have fast oscillations that helps us get rid of one or both of the frequency integrals even for the broad class of spectral densities we are considering. For the terms that do not have time dependence, the expression cannot be further simplified because we have not assumed a specific form of the spectral density. Hence, our final expressions for the TCL4 coefficients contain at most double frequency integrals, which can be easily evaluated numerically or analytically for any specific choice of spectral density.

Finally, these integrals are evaluated as,

$$\begin{aligned} F_{33}^{(4)} = & \frac{1}{2} \int_{-\infty}^{\infty} d\omega \left\{ \frac{4\pi a_1^4 \Omega f(\omega)}{(\omega^2 - \Omega^2)^2} \left[ (\omega^2 - \Omega^2) f'(\Omega) + 2\Omega f(\Omega) \right] \right. \\ & + \frac{2\pi a_1^2 a_3^2}{(\omega^3 - \omega\Omega^2)^2} \left[ f(\omega) \left( 4f(\Omega) (\omega^2 - \Omega^2)^2 \right. \right. \\ & \quad - 2\omega\Omega(\omega + \Omega)^2 f(\omega - \Omega) + \omega(\omega - \Omega) (2\Omega(\omega - \Omega) f(\omega + \Omega) \\ & \quad \left. \left. - 4f(0)\omega(\omega + \Omega)) \right) \right. \\ & \quad \left. \left. - 2\Omega J(\omega) (\omega^2 - \Omega^2) ((\omega + \Omega)J(\omega - \Omega) + (\Omega - \omega)J(\omega + \Omega)) \right) \right] \Bigg\}, \quad (3.35) \end{aligned}$$

$$\begin{aligned}
F_{30}^{(4)} = \frac{1}{2} \int_{-\infty}^{\infty} d\omega & \left\{ \frac{4\pi a_1^4}{(\omega^2 - \Omega^2)^2} \left[ f(\omega) (\Omega(\omega^2 - \Omega^2) J'(\Omega) \right. \right. \\
& + J(\Omega) (\omega^2 + 3\Omega^2)) - 2\omega\Omega f(\Omega) J(\omega) \Big] + \frac{4\pi a_1^2 a_3^2}{(\omega^3 - \omega\Omega^2)^2} \\
& \times \left[ 2f(0)\omega\Omega J(\omega) (\Omega^2 - \omega^2) + f(\omega) ( \right. \\
& \left. \left. (\omega - \Omega)^2 (2J(\Omega)(\omega + \Omega)^2 - \Omega^2 J(\omega + \Omega)) + \Omega^2 (\omega + \Omega)^2 J(\omega - \Omega) \right) \right] \Big\}, \tag{3.36}
\end{aligned}$$

where, the contour for these integrals (Eq. (3.35) and Eq. (3.36)) are defined to go above any pole on the real line (see Fig. 3.1), hence not including the contribution of the poles at the real line and also avoiding the corresponding apparent divergences (See Sec. 3.4.3 for details). We note that unlike the general expression for the TCL4 coefficients given in Eq. (3.34), the final expressions for the TCL4 coefficients given in Eq. (3.35) and Eq. (3.36) *do not* contain any double frequency integrals. Since our results are for a broad class of  $J(\omega)$ , these expressions cannot be reduced any further.

Using the expression for the second order SS population (Eq. (3.29)), we have

$$\begin{aligned}
v_3^{(2)} = -2a_1^2 \tanh\left(\frac{\beta\Omega}{2}\right) \int_0^\infty d\omega \frac{J(\omega)}{(\omega^2 - \Omega^2)^2} & \left[ \right. \\
2\omega\Omega \coth\left(\frac{\beta\Omega}{2}\right) - \coth\left(\frac{\beta\omega}{2}\right) (\beta\Omega(\omega^2 - \Omega^2) \text{csch}(\beta\Omega) + \omega^2 + \Omega^2) & \left. \right]. \tag{3.37}
\end{aligned}$$

This matches with the MFGS value of  $v_3^{(2)}$  [22]. We have hence analytically shown that for the generic SBM, all second order SS components match with the corresponding MFGS corrections. Also, equipped with analytical expression for the TCL4 generator, we have also evaluated the 4th order corrections to the SS coherences. See the Supplemental Material [52] for all these results in electronic form.

In Sec. 3.4.5, we also provide the values of the TCL2 and TCL4 generators for a special choice of spectral density well studied in literature, namely the Ohmic spectral density with Drude cutoff (Eq. (2.89)). For this spectral density, the expressions for the two-

point correlation functions  $\nu(t)$  and  $\eta(t)$  are known in closed form, hence assisting in the evaluation of the TCL4 generator matrix elements. The calculations thus proceed differently than those for the general case, but we have verified that both the results are consistent with each other (see Sec. 4.3.1 for details).

**Comparison with related works:** Here, we note how our results presented here differ from those of Crowder et al. [11]. The expression for the asymptotic TCL4 generator obtained by Crowder et al. still has an infinite time integral, which is not the case for our result. Consequently, they have numerically demonstrated the equivalence between the second order SS and MFGS at zero temperature, whereas our result is analytical one and is valid at arbitrary non-zero temperature. Also, their results were derived under the assumption that the spectral density is of the form  $J(\omega) = C\omega^s \exp(-\omega/\omega_c)\Theta(\omega)$  (here  $C, s > 0$  are some constant and  $\Theta(\omega)$  is Heaviside step-function). Whereas our results are valid for all single valued, odd spectral densities that decay at least as  $1/\omega$  in large  $\omega$  limit (see Sec. 3.3.1). We do note that their work is valid for a generic  $N$  dimensional system, whereas we have restricted ourselves to the generic SBM (two level system).

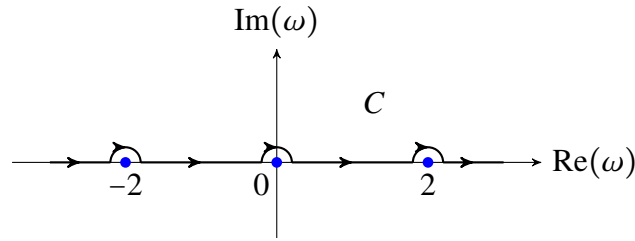


Figure 3.1: Pictorial representation of the convention for the contour to be taken for the frequency integrals in the final expressions for the TCL4 generator matrix elements (Eq. (3.35) and Eq. (3.36)). The contour has to be assumed to go above the poles on the real line (represented here as blue dots). This convention is just for convenience and is a natural consequence of how the TCL4 calculations are carried out here.

## 3.3 Assumptions and regime of validity

### 3.3.1 Assumption on the spectral density

In this section, we discuss the assumptions we made on the spectral density to carry out our calculations, which will become clear as we discuss the details of the calculations in Secs. 3.4.3 and 3.4.4. These are:

1. *Odd function*:  $J(\omega)$  is an analytical function which can be analytically continued to the negative values of  $\omega$  as an odd function ( $J(\omega) = -J(-\omega)$ ). This implies that the integrand (Eq. (3.33)) is even in frequency, allowing us to extend the integration to negative frequencies, which simplifies our calculations.
2. *Single valued function*: We assume this to avoid any branch cuts that may appear while extending the contour to the complex plane.
3. *Frequency cutoff*:  $J(\omega)$  decays at least as  $1/\omega$  in the large- $\omega$  limit to ensure convergence of the integral. We note that this condition can be further relaxed, but we restrict ourselves to physical spectral densities by assuming it.

### 3.3.2 Existence of asymptotic Time-Convolutionless generator

Lampert et al. [12] have recently reported that the asymptotic TCL generator may not always exist. This is specifically the case for  $\text{TCL}2n$  for  $n > n_{\text{max}}$  for some finite  $n_{\text{max}}$ , when the correlation function (Eq. (3.22) and Eq. (3.23)) asymptotically decays as an algebraic function. For the correlation function with exponential asymptotic decay, though, they have found that the TCL generator converges provided the coupling remains below a critical threshold.

We note that in our case, the correlation functions indeed decay exponentially in the

asymptotic limit. In the integrals for the correlation function (Eq. (3.22) and Eq. (3.23)), we expand the sine and cosine in terms of exponentials,  $e^{+i\omega t}$  and  $e^{-i\omega t}$ . For oscillations with positive sign (i.e.,  $e^{+i\omega t}$ ), we draw a contour from  $\omega = +\infty$  to  $\omega = -\infty$  in the upper half-plane, running just above the real axis such that it does not go through any poles that the integrand may have in the upper plane. This contour is not restricted to the shape of a large semi-circle; any path strictly in the upper half-plane that does not pass through a pole is sufficient. Then, we can express the integral as the sum of the integral along this contour and the contributions from any enclosed poles.

Note now that although  $\coth(\beta\omega/2)$  has a pole at  $\omega = 0$ , from condition (1),  $J(0) = 0$ , so this pole will not contribute. Also, note that physically,  $J(\omega)$  itself cannot have any poles for  $\omega \geq 0$ . We can also see this mathematically from the fact that  $J(\omega) \geq 0$ , which rules out odd-order poles; even-order poles would lead to divergences in the two-point correlation function integral (Eq. (3.22) and Eq. (3.23)). This rules out any non-exponentially decaying oscillations in the asymptotic limit. Next, from condition (2), since all the functions involved are single-valued, there are no extra complications regarding branch cuts. Additionally, from condition (3), the integrals near  $\omega = \pm\infty$  are convergent.

Hence, in the large  $t$  limit, both the residues from the enclosed poles and the integral along the upper-plane contour will have exponentially decaying behavior. A similar argument can be repeated for oscillations with a negative sign (i.e.,  $e^{-i\omega t}$ ). Therefore, for the class of spectral density considered by us, the asymptotic TCL generators are well defined, as long as the SE coupling strength is sufficiently small to allow for the validity of the TCL formalism itself [3, 12].

### 3.3.3 Zero Temperature limit

The asymptotic TCL generator is valid on a timescale  $t \gg \max\{\Lambda^{-1}, \beta/(2\pi)\}$ . Hence, at *exactly* zero temperature, since  $\beta = \infty$ , the asymptotic TCL generator becomes unphysical because we will need to wait for an infinite time for it to become physically relevant. Also, at  $T = 0$ , the function  $\coth(\beta\omega/2)$  has poles at every point on the imaginary axis ( $\omega = ix$  for  $x \in \mathbb{R}$ ), which would make the use of standard techniques like contour integration problematic. It may be noted that for a certain class of spectral density (different from ours), TCL4 and steady state calculations at zero temperature have been performed by Crowder et al. [11].

Hence, our results are only valid for arbitrary non-zero temperature, given that the SE coupling strength is correspondingly small enough to allow for the validity of TCL formalism [3]. One test for the validity of our results, in any parameter regime including low temperatures, would be the norm ratio of the TCL4 and TCL2 generators [13], which is expected to be much less than one when TCL4 is applicable.

## 3.4 Technical Details

### 3.4.1 Some steady state and mean force Gibbs state results for generic open quantum system

Here, we summarize some results valid for a generic open-quantum system at arbitrary SE coupling. This will help simplify the accompanying TCL2 and TCL4 calculations and also identify some generic features in the SS and the TCL generator.

For a generic open quantum system, not necessarily for a qubit system or Bosonic envir-

onment or weak coupling, let the full SE Hamiltonian be given as

$$\hat{H}_{SE} = \hat{H}_S + \hat{H}_E + \hat{H}_I, \quad (3.38)$$

$$\hat{H}_I = \lambda \hat{A} \otimes \hat{B}, \quad (3.39)$$

where  $\hat{A}$  and  $\hat{B}$  are system and environment operators, respectively.

For a generic operator  $\hat{O}$  in Schrodinger picture, the corresponding Heisenberg picture operator is defined as [3]

$$\hat{O}_H(t) = e^{it\hat{H}_{SE}} \hat{O} e^{-it\hat{H}_{SE}}, \quad (3.40)$$

and the corresponding equation of motion is given as

$$\frac{d}{dt} \hat{O}_H(t) = i[\hat{H}_{SE}, \hat{O}_H(t)] + \left( \frac{\partial \hat{O}}{\partial t} \right)_H. \quad (3.41)$$

Assuming that  $\hat{O}$  is time independent (that is, in the Schrodinger picture, we have  $\partial \hat{O} / \partial t = 0$ ). Then the equation of motion for  $\hat{O}_H(t)$  simplifies as

$$\frac{d}{dt} \hat{O}_H(t) = i[\hat{H}_{SE}, \hat{O}_H(t)], \quad (3.42)$$

$$= ie^{it\hat{H}_{SE}} [\hat{H}_{SE}, \hat{O}] e^{-it\hat{H}_{SE}}. \quad (3.43)$$

Next, let us have, for some system operator  $\hat{O}_1$ ,

$$[\hat{O}_1, \hat{A}] \equiv 0. \quad (3.44)$$

Then, in Eq. (3.43), we have

$$\frac{d}{dt} \hat{O}_{1,H}(t) = ie^{it\hat{H}_{SE}} [\hat{H}_S, \hat{O}_1] e^{-it\hat{H}_{SE}}, \quad (3.45)$$

$$\implies \frac{d}{dt} \langle \hat{O}_{1,H}(t) \rangle = \text{Tr} \{ -i[\hat{O}_1, \hat{H}_S] \hat{\rho}_{SE}(t) \}. \quad (3.46)$$

Hence, in the large time limit, we have

$$\frac{d}{dt} \langle \hat{O}_1 \rangle_{\hat{\rho}_S(t)} = 0 = \lim_{t \rightarrow \infty} \text{Tr} \{ -i [\hat{O}_1, \hat{H}_S] \hat{\rho}_{SE}(t) \}. \quad (3.47)$$

Defining

$$\hat{O}_2 \equiv [\hat{O}_1, \hat{H}_S], \quad (3.48)$$

for a generic open quantum system with a SS, we then have that,

$$\langle \hat{O}_2 \rangle_{SS} = 0. \quad (3.49)$$

### Consistency with mean force Gibbs state

We will now prove that for the MFGS at arbitrary SE coupling, we correspondingly have that

$$\langle \hat{O}_2 \rangle_{MF} = 0. \quad (3.50)$$

*Proof.* We have,

$$\langle \hat{O}_2 \rangle_{MF} \equiv \text{Tr}_S \{ \hat{O}_2 \hat{\rho}_{MF} \}, \quad (3.51)$$

$$= \text{Tr}_S \{ \hat{O}_2 Z^{-1} \text{Tr}_E \exp \{ -\beta \hat{H}_{SE} \} \}, \quad (3.52)$$

$$= \text{Tr} \left\{ \hat{O}_2 \sum_{n=0}^{\infty} \frac{1}{n! Z} (-\beta)^n \hat{H}_{SE}^n \right\}, \quad (3.53)$$

$$= \sum_{n=0}^{\infty} \frac{1}{n! Z} (-\beta)^n \text{Tr} \{ \hat{O}_2 \hat{H}_{SE}^n \}, \quad (3.54)$$

$$= \sum_{n=0}^{\infty} \frac{1}{n! Z} (-\beta)^n \text{Tr} \{ [\hat{O}_1, \hat{H}_S] \hat{H}_{SE}^n \}, \quad (3.55)$$

In Sec. 3.4.1, we prove that, for any operators  $\hat{O}, \hat{S}$  and  $\hat{J}$ , given that  $[\hat{O}, \hat{J}] = 0$ , we have

$$\text{Tr} \{ [\hat{O}, \hat{S}] (\hat{S} + \hat{J})^N \} = 0. \quad (3.56)$$

where,  $N$  is a whole number. Writing  $\hat{O} \rightarrow \hat{O}_1$ ,  $\hat{S} \rightarrow \hat{H}_S$  and  $\hat{J} \rightarrow \hat{H}_E + \hat{H}_I$ , we observe that we do have  $[\hat{O}_1, \hat{H}_E + \hat{H}_I] = 0$ . Hence, we get,

$$\text{Tr} \{ [\hat{O}_1, \hat{H}_S] (\hat{H}_S + \hat{H}_E + \hat{H}_I)^N \} = 0, \quad (3.57)$$

$$\implies \text{Tr} \{ \hat{O}_2 \hat{H}_{SE}^n \} = 0 \quad (3.58)$$

$$\implies \langle \hat{O}_2 \rangle_{MF} = 0. \quad (3.59)$$

□

We note that for a  $d$  dimensional system, there are generally  $d$  orthogonal operators  $\hat{O}_1$  that commute with  $\hat{A}$ , of which one is trivially the identity operator. Each of the remaining nontrivial operators  $\hat{O}_1$  has a corresponding operator  $\hat{O}_2$  for which the correspondence between MFGS and SS holds (Eq. (3.49) and Eq. (3.59)). Hence, although the general results on the limits on the SE coupling strength  $\lambda$  and temperature  $T$  for which the equivalence between SS and MFGS holds, are not available [5, 23–31], for the expectation values of the class of operators,  $\hat{O}_2$ , at least, we have just proven that the equivalence exists for the entire range of SE parameters. For example, it can be verified that  $\langle \hat{O}_2 \rangle_{MF} = 0$  even for known analytical expression for the ultrastrong coupling MFGS [22, 87].

### Proof of the commutation identity

**Proposition 4.** *Given*

$$[\hat{O}, \hat{J}] = 0, \quad (3.60)$$

to prove that

$$\text{Tr} \{ [\hat{O}, \hat{S}] (\hat{S} + \hat{J})^N \} = 0. \quad (3.61)$$

where  $N$  is a whole number.

*Proof.* We have

$$\text{Tr} \{ [\hat{O}, \hat{S}] (\hat{S} + \hat{J})^N \} \equiv T_1 - T_2, \quad (3.62)$$

where

$$T_1 = \text{Tr} \{ \hat{O} \hat{S} (\hat{S} + \hat{J})^N \}, \quad (3.63)$$

$$T_2 = \text{Tr} \{ \hat{S} \hat{O} (\hat{S} + \hat{J})^N \}. \quad (3.64)$$

Each of  $T_1$  and  $T_2$  will have  $2^N$  total number of terms, with each term expressed as a trace over the product of  $N + 2$  operators. The idea is that, for every term in  $T_1$ , let us call it  $e_1$ , we need to find a cyclically equivalent unique term in  $T_2$ , which we will call  $e_2$ , and which will cancel it under trace (in Eq. (3.62)).

Let us symbolically represent the terms,  $e_1$  and  $e_2$ , as

$$e_1 = \text{Tr} \{ \hat{O} \hat{S} X_1 \dots X_N \}, \quad (3.65)$$

$$e_2 = \text{Tr} \{ \hat{S} \hat{O} Y_1 \dots Y_N \}. \quad (3.66)$$

Here,  $X_i, Y_i \in \{\hat{S}, \hat{J}\}$ . Also, for mathematical convenience, let us define  $X_0 = Y_0 = \hat{S}$ .

Then, the above expression transform as

$$e_1 = \text{Tr} \{ \hat{O} X_0 X_1 \dots X_N \}, \quad (3.67)$$

$$e_2 = \text{Tr} \{ Y_0 \hat{O} Y_1 \dots Y_N \}. \quad (3.68)$$

Then, for a given choice of  $X_i$ , let  $0 \leq k \leq N$  be the largest integer such that  $X_k = \hat{S}$ . Note that there will always be a solution for  $k$  because  $X_0 = \hat{S}$  (hence,  $k = 0$  is always a possible solution).

Next, by definition of  $k$ , for  $n > k$ ,  $X_n = \hat{J}$ . Hence,  $e_1$  has the form

$$e_1 = \text{Tr} \{ \hat{O} X_0 \dots X_{k-1} \hat{S} \hat{J} \hat{J} \dots (N - k \text{ times}) \}. \quad (3.69)$$

Using cyclic rotation under trace and the fact that  $\hat{O}$  commutes with  $\hat{J}$  (Eq. (3.60)), we get,

$$e_1 = \text{Tr} \{ \hat{S} \hat{O} \hat{J} \hat{J} \dots (N - k \text{ times}) X_0 \dots X_{k-1} \}, \quad (3.70)$$

$$= \text{Tr} \{ X_k \hat{O} X_{k+1} \dots X_N X_0 \dots X_{k-1} \}, \quad (3.71)$$

$$\equiv \text{Tr} \{ Y_0 \hat{O} Y_1 \dots Y_N \}, \quad (3.72)$$

$$= e_2. \quad (3.73)$$

That is, going from Eq. (3.71) to Eq. (3.72) defines the map between  $X_i$  and  $Y_j$  that is required to go from  $e_1$  to  $e_2$ . That is, we used the relation  $Y_0 = X_k, Y_1 = X_{k+1} \dots Y_{N+1-k} = X_0 \dots Y_N = X_{k-1}$ . More formally, this map is given by

$$Y_{n(\text{mod}(N+1))} \equiv X_{(n+k)(\text{mod}(N+1))}. \quad (3.74)$$

Next we must prove that this map is bijective. Eq. (3.74) is inherently a bijective function, but there is one nontriviality. The integer  $k$  is defined given  $e_1$  and we need a procedure to determine it given  $e_2$ . Once we know  $k$  given  $e_2$ , then the corresponding  $e_1$  can similarly be determined through ‘the reverse cyclic shift’ as

$$X_{n(\text{mod}(N+1))} \equiv Y_{(n-k)(\text{mod}(N+1))}. \quad (3.75)$$

We note that going from Eq. (3.70) to Eq. (3.73) involves variable renaming and no further

operator manipulation. Hence, Eq. (3.70) is essentially the expression for  $e_2$ . To identify the value of  $k$  from here, we just count the number of consecutive  $\hat{J}$ 's to the right of  $\hat{O}$ , which is numerically equal to  $N-k$  (see Eq. (3.70)). The value of  $k$  can thus be determined, allowing us to determine the inverse map and proving the bijectivity.

**Summary:** We have proved that for every  $e_1$ , there exists a  $e_2$  such that  $e_1 = e_2$ , and vice versa. In Eq. (3.62), these two terms,  $e_1$  and  $e_2$ , are going to cancel each other out, which proves our final result (Eq. (3.61)).  $\square$

### 3.4.2 TCL2 integrals and their solution

The matrix element of the TCL2 generator  $F^{(2)}(t)$  can be evaluated as [3, 94]

$$F_{10}^{(2)}(t) = \int_0^t 4a_1 a_3 \eta(t-t_1) \sin((t-t_1)\Omega) dt_1, \quad (3.76)$$

$$F_{11}^{(2)}(t) = \int_0^t -4a_3^2 \nu(t-t_1) dt_1, \quad (3.77)$$

$$F_{12}^{(2)}(t) = 0, \quad (3.78)$$

$$F_{13}^{(2)}(t) = \int_0^t -4a_1 a_3 \nu(t-t_1) \cos((t-t_1)\Omega) dt_1, \quad (3.79)$$

$$F_{20}^{(2)}(t) = \int_0^t -4a_1 a_3 \eta(t-t_1) (\cos((t-t_1)\Omega) - 1) dt_1, \quad (3.80)$$

$$F_{21}^{(2)}(t) = \int_0^t 4a_1^2 \nu(t-t_1) \sin((t-t_1)\Omega) dt_1, \quad (3.81)$$

$$F_{22}^{(2)}(t) = \int_0^t -4\nu(t-t_1) (a_1^2 \cos((t-t_1)\Omega) + a_3^2) dt_1, \quad (3.82)$$

$$F_{23}^{(2)}(t) = \int_0^t -4a_1a_3\nu(t-t_1) \sin((t-t_1)\Omega) dt_1. \quad (3.83)$$

Here, we specify only 8 of the 16 matrix elements of the TCL2 generator matrix explicitly because the remaining elements are either zero or can be obtained from these using certain symmetries, as we discussed in Sec. 3.1.2.

Next, we solve these integrals assuming an arbitrary spectral density  $J(\omega)$ , and get a general expression for the TCL2 matrix elements as,

$$F_{10}^{(2)} = -2\pi a_1 a_3 J(\Omega), \quad (3.84)$$

$$F_{11}^{(2)} = -2\pi a_3^2 f(0), \quad (3.85)$$

$$F_{13}^{(2)} = -2\pi a_1 a_3 f(\Omega), \quad (3.86)$$

$$F_{20}^{(2)} = \int_0^\infty -\frac{4a_1a_3\Omega^2 J(\omega)}{\omega(-\omega^2 + \Omega^2)} d\omega, \quad (3.87)$$

$$F_{21}^{(2)} = \int_0^\infty \frac{4a_1^2\Omega f(\omega)}{-\omega^2 + \Omega^2} d\omega, \quad (3.88)$$

$$F_{22}^{(2)} = -2\pi a_1^2 f(\Omega) - 2\pi a_3^2 f(0), \quad (3.89)$$

$$F_{23}^{(2)} = \int_0^\infty -\frac{4a_1a_3\Omega f(\omega)}{-\omega^2 + \Omega^2} d\omega. \quad (3.90)$$

Again, the remaining matrix elements are zero or can be obtained from these as discussed in Sec. 3.1.2.

### 3.4.3 Technical Details of TCL4 integral evaluation

We will now discuss in detail the evaluation of one of the TCL4 integrals,  $F_{33}^{(4)}(t)$ . See Eq. (3.30) for the full definition. We focus on the simpler case when  $a_3 = 0$  and  $a_1 = 1/2$ . We first expand the integrand of Eq. (3.30) using the definition of  $v(t)$  given in terms of an integral over  $\omega$  (Eq. (3.23)). Since we have assumed an antisymmetric spectral density,  $J(\omega)$ , this means that  $f(\omega)$  (Eq. (3.24)) is symmetric. Hence, we can extend the integration limit of  $\omega$  from  $(0, +\infty)$  to  $(-\infty, +\infty)$  and multiply a factor of  $1/2$  to get the following expression for  $F_{33}^{(4)}$ ,

$$F_{33}^{(4)} = \lim_{t \rightarrow \infty} \frac{1}{4} \int_{-\infty}^{\infty} d\omega_2 \int_{-\infty}^{\infty} d\omega_1 \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 f(\omega_1) f(\omega_2) \\ \times \left\{ \cos((t-t_2)\omega_1) \cos((t_1-t_3)\omega_2) \sin((t_1-t_2)\Omega) \sin((t-t_3)\Omega) \right. \\ \left. + \cos((t-t_3)\omega_1) \cos((t_1-t_2)\omega_2) \sin((t-t_2)\Omega) \sin((t_1-t_3)\Omega) \right\}. \quad (3.91)$$

After analytically doing the triple time integral for arbitrary spectral density  $J(\omega)$ , which can be easily done using a computer algebra system like Mathematica, we are then left with the remaining  $\omega_1$  and  $\omega_2$  integrals. The integrand now has the following form,

$$F_{33}^{(4)} = \lim_{t \rightarrow \infty} \int_{-\infty}^{\infty} d\omega_2 \int_{-\infty}^{\infty} d\omega_1 \sum_{m_1, m_2=-1}^1 D_{m_1, m_2}(\omega_1, \omega_2) e^{it(m_1\omega_1 + m_2\omega_2)}. \quad (3.92)$$

#### General procedure to evaluate the frequency integrals

In order to systematically evaluate these integrals, we employ a symbolic algorithm that performs the following steps. For each of the 9 possible combinations of  $m_1, m_2$ , it first performs the  $\omega_1$  integral, followed by the  $\omega_2$  integral. Each of these frequency integrals

$\omega \in \{\omega_1, \omega_2\}$ , with  $m \in \{m_1, m_2\}$ , is performed in the following manner, illustrated in Fig. 3.2. First, we express the  $\omega$  integral in terms of contributions from the real poles  $X_i$  on the real line. The remaining contribution of the  $\omega$  integral is expressed in terms of a contour  $C$  lifted strictly above the real line for  $m \in \{1, 0\}$  and below the real line for  $m \in \{-1\}$ . For simplicity, we choose  $C$  such that it does not enclose any pole strictly in the complex plane (like for  $m = 0, 1$  in Fig. 3.2a,  $C$  passes the red point  $P_1$  from below, while for  $m = -1$  in Fig. 3.2b,  $C$  passes the red point  $P_2$  from above).

The motivation for this procedure of choosing the contour  $C$  for different values of  $m$  is that for  $m \neq 0$ , the corresponding  $e^{im\omega t}$  factor will cause the corresponding contour  $C$  to have zero contribution. For the  $m = 0$  case, we could choose  $C$  to pass from either above or below. We choose the former convention to make the results in the symbolic algorithm easier to track.

We note that for  $m \neq 0$ , since the contour integral over  $C$  vanishes in the large  $t$  limit, the corresponding  $\omega$  integral can be evaluated without knowing the expression for the spectral density. On the other hand, for  $m = 0$ , the contour integral over  $C$  remains, which cannot be further simplified without knowing the form of the spectral density. Since these contour integrals for  $m = 0$  pass the real axis from above under our convention, this explains why we have the same convention for all the TCL4 results as mentioned earlier in Sec. 3.2 and illustrated in Fig. 3.1.

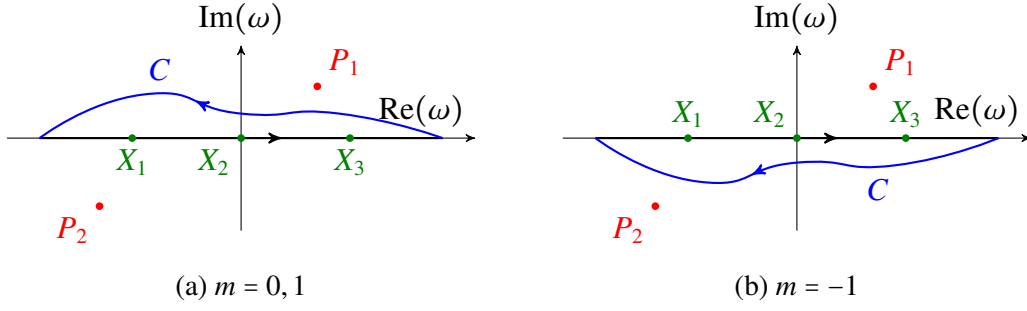


Figure 3.2: Contours  $C$  used to lift the original  $\omega$  integration contour in Eq. (3.92): (a) into the upper half-plane for  $m = 0, 1$ , excluding  $P_1$ , and (b) into the lower half-plane for  $m = -1$ , excluding  $P_2$ . This systematic procedure of completing the contour for the two frequency integrals  $\omega = \omega_1, \omega_2$  and time oscillation factors  $m = m_1, m_2$  is adopted so that in the large  $t$  limit, the contribution of the contour integral over  $C$  gives vanishing result for  $m \neq 0$ .

### Detailed evaluation of $F_{33}^{(4)}$

For the present example, we note that the  $D_{0,0}$  term is zero, although that might not always be the case. However, the  $m_1 = m_2 = 0$  term cannot be further simplified for a general spectral density and is also time independent.

For  $m_1 = \pm 1$ , this procedure yields:

$$\lim_{t \rightarrow \infty} \int_{-\infty}^{\infty} d\omega_2 \int_{-\infty}^{\infty} d\omega_1 \sum_{m_1=\pm 1} \sum_{m_2=-1}^1 D_{m_1, m_2}(\omega_1, \omega_2) e^{it(m_1\omega_1 + m_2\omega_2)} = \frac{1}{2} \int_{-\infty}^{\infty} d\omega \frac{\pi \Omega f(\omega) f'(\Omega)}{4\omega^2 - 4\Omega^2}. \quad (3.93)$$

Again, we note that the  $\omega$  integral above passes any real poles from above, by convention.

Next, the  $m_1 = 0$  case is more complicated as the corresponding contour integral over  $C$  survives. For brevity, we replace  $m_2 = m$  and write

$$\int_{-\infty}^{\infty} d\omega_1 \sum_{m=\pm 1} D_{0, m}(\omega_1, \omega_2) e^{itm\omega_2} = \sum_{m=\pm 1} \left( \pi i R_m(\omega_2) e^{itm\omega_2} - \int_C D_{0, m}(z, \omega_2) e^{itm\omega_2} dz \right). \quad (3.94)$$

Here,  $R_m(\omega_2)$  is, for a fixed value of  $\omega_2$ , the sum of the residues of the poles of the

function  $D_{0,m}(\omega_1, \omega_2)$  at real values of  $\omega_1$  (see Fig. 3.2). Here, the expression for the sum over residues,  $R_m(\omega_2)$ , is expressed symbolically because we have not assumed any functional form of the spectral density,  $J(\omega)$ .

Next, since  $D_{0,0} = 0$ , as mentioned before, the remaining  $\omega_2$  integral can be evaluated analytically because in the large  $t$  limit, only the poles at the real value of  $\omega_2$  will contribute. Once the  $\omega_2$  variable is eliminated in this manner, the integrand becomes a function of  $\omega_1$  in the form of a finite scalar and as an integral over the contour  $C$ .

In more detail, let  $\omega_2$  equal to  $c_i$  and  $d_i$  be the real values at which the function  $R_m(\omega_2)$  and  $D_{0,m}(z, \omega_2)$  have poles, respectively. Here, the corresponding residue functions are symbolically denoted as  $\bar{R}_m(c_i)$  and  $\bar{D}_{0,m}(z, d_i)$ , respectively. Then, for  $m = 1$  in Eq. (3.94), for example, we have,

$$\int_{-\infty}^{\infty} d\omega_2 \int_{-\infty}^{\infty} d\omega_1 D_{0,1}(\omega_1, \omega_2) e^{it\omega_2} = \pi i \sum_i \left( \pi i \bar{R}_1(c_i) e^{itc_i} - \int_C \bar{D}_{0,1}(z, d_i) e^{itd_i} dz \right). \quad (3.95)$$

We note that the only integral now left is over a contour  $C$  (Fig. 3.2) which cannot be further simplified. Keeping this in mind that this integral avoids any poles on the real line by passing it from above (see Fig. 3.1), after renaming  $\omega_1 \rightarrow \omega$ , the final result comes out as

$$\int_0^{\infty} d\omega_2 \int_0^{\infty} d\omega_1 \sum_{m=\pm 1} D_{0,m}(\omega_1, \omega_2) e^{itm\omega_2} = \frac{1}{2} \int_{-\infty}^{\infty} d\omega \frac{\pi \Omega^2 f(\omega) f(\Omega)}{2(\omega^2 - \Omega^2)^2}. \quad (3.96)$$

Combining Eq. (3.96) and Eq. (3.93), we have,

$$F_{33}^{(4)} = \frac{\pi \Omega}{4} \int_{-\infty}^{\infty} d\omega \left( \frac{f(\omega) f'(\Omega)}{2\omega^2 - 2\Omega^2} + \frac{\Omega f(\omega) f(\Omega)}{(\omega^2 - \Omega^2)^2} \right) \quad (3.97)$$

which agrees with Eq. (3.35) for  $a_3 = 0$  and  $a_1 = 1/2$ . The expression of  $F_{33}^{(4)}$  for general values of  $a_1$  and  $a_3$  and also the corresponding expression for  $F_{30}^{(4)}$  can similarly be evaluated using exactly the same steps mentioned here, as we explicitly show in the Sup-

plementary Material [52].

### 3.4.4 Dependence of the integral on the order of the integration

The procedure to evaluate the frequency integrals in Sec. 3.4.3 is quite systematic yet complicated. This begs the question: Can we simplify it? For example, for  $m_1 \neq 0$ , the integral is quite simple because the contour  $C$  does not contribute and hence the  $\omega_1$  integral breaks down into a sum over contributions from the real poles. But for  $m_1 = 0$ , the contour integral over  $C$  survives, and the procedure is slightly more complicated. What if, for  $m_2 \neq 0$ , we perform the  $\omega_2$  integral first, which, by symmetry, will be easier to evaluate? It turns out that this exchange of the order of integrals gives rise to discrepancies and divergent results. That is, we need to choose one order of the frequency integral and stick with it throughout the procedure.

#### Illustrative example

Before diving into the details of this specific situation, let us illustrate the nature of the discrepancy through an example. Let us define

$$Q_1(f) \equiv \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy f(x, y) \quad (3.98)$$

$$Q_2(f) \equiv \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dx f(x, y) \quad (3.99)$$

$$S(f) \equiv Q_1(f) - Q_2(f) \quad (3.100)$$

Here,  $Q_i$  and  $S$  are functionals of  $f$ . Next, let us say we are interested in evaluating the integral

$$I \equiv \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy [g(x, y) + h(x, y)] \quad (3.101)$$

$$= Q_1(g + h) \quad (3.102)$$

where, the functions  $g(x, y)$  and  $h(x, y)$  are *defined* such that we have

$$S(g) \equiv -S(h) \neq 0 \quad (3.103)$$

That is, they both individually violate Fubini's theorem [110] but under the constraint given in Eq. (3.103). Then, for the sum of these two functions (i.e.,  $g(x, y) + h(x, y)$ ), the discrepancy disappears as following

$$S(g + h) = S(g) + S(h) = 0. \quad (3.104)$$

Moreover, replacing the definition of  $S$  in Eq. (3.103), we get

$$Q_1(g) - Q_2(g) = -Q_1(h) + Q_2(h) \quad (3.105)$$

$$\implies Q_1(g) + Q_1(h) = Q_2(h) + Q_2(g) \quad (3.106)$$

$$\implies I = Q_1(g + h) = Q_2(g + h) \quad (3.107)$$

That is, the order in which the integral is carried out does not matter as long as it is done in the same order for both the individual terms  $g$  and  $h$ .

Next, also note that if we are not consistent with the order of integration for both the individual terms, then we will encounter a discrepancy as following

$$Q_1(h) + Q_2(g) \neq Q_1(h + g). \quad (3.108)$$

In the case of the TCL4 integral, we encounter something similar.

## Specific details

For  $m_1 = 0$  and  $m_2 = 1$  in the original integrand (Eq. (3.92)), for example,  $D_{0,1}(\omega_1, \omega_2)e^{it\omega_2}$  has the precise form given as

$$D_{0,1}(\omega_1, \omega_2)e^{it\omega_2} = \frac{\omega_2 \Omega f(\omega_1) f(\omega_2) e^{it\omega_2} (-\omega_2 \sin(t\Omega) - i\Omega \cos(t\Omega))}{2(\omega_1^2 - \omega_2^2)(\Omega^2 - \omega_1^2)(\Omega^2 - \omega_2^2)}. \quad (3.109)$$

Note that since  $f(\omega)$  is a symmetric function, the integrand is symmetric in  $\omega_1$  but not so in  $\omega_2$ . We have already discussed how to proceed if we do the  $\omega_1$  integral first using the contour  $C$  represented in Fig. 3.2. We note that due to symmetry, the poles for  $\omega_1$  at  $\pm\omega_2$  and  $\pm\Omega$  do not contribute to the integral ( $R_m(\omega_2) = 0$  in Eq. (3.94)). Hence, the  $\omega_1$  integral is transformed as just an integral over the contour  $C$  (Fig. 3.2). Afterwards, when we do the  $\omega_2$  integral, in large  $t$  limit, only the poles at the real values of  $\omega_2$  will contribute to the integral. The only real poles that remain are for  $\omega_2 = \pm\Omega$ . This is because on the contour  $C$ ,  $\omega_1$  now attains a positive imaginary value, and hence the poles at  $\omega_2 = \pm\omega_1$  have been lifted from the real axis of  $\omega_2$ .

On the other hand, if we try the  $\omega_2$  integral first, then the real poles at  $\omega_2 = \pm\Omega$  will give the exact same result as the integral before. But unlike in the last case, there will be some extra terms because of the poles at  $\omega_2 = \pm\omega_1$  that were not there earlier. In fact, these extra terms give divergent contributions in the large  $t$  limit, which is the limit we are interested in.

For this reason, we need to be consistent with the choice of the order of integration over the variables  $\omega_1$  and  $\omega_2$  for all the terms in the original integrand (Eq. (3.92)). In other words, it does not matter whether we integrate  $\omega_1$  first or  $\omega_2$ , but we need to be consistent with this choice for all terms.

Now, we will explicitly calculate the extra divergent term that we get when we do the  $\omega_2$

integral first in Eq. (3.109). This comes from the  $\omega_2 = \pm\omega_1$  poles, which contribute

$$\begin{aligned} \text{Extra Term} = \pi i \int_{-\infty}^{\infty} d\omega_1 & \left[ \frac{i\Omega f(\omega_1)^2 e^{-it\omega_1} (\Omega \cos(t\Omega) + i\omega_1 \sin(t\Omega))}{4(\Omega^2 - \omega_1^2)^2} \right. \\ & \left. + \frac{\Omega f(\omega_1)^2 e^{it\omega_1} (\omega_1 \sin(t\Omega) + i\Omega \cos(t\Omega))}{4(\Omega^2 - \omega_1^2)^2} \right] \end{aligned} \quad (3.110)$$

The  $\omega_1$  contour for  $e^{-it\omega_1}$  and  $e^{it\omega_1}$  will be completed from below and above, respectively, with only the poles at  $\omega_1 = \pm\Omega$  at the real line contributing to the  $\omega_1$  integral in the large  $t$  limit. This gives

$$\text{Extra Term} = -\frac{\pi^2 f(\Omega)^2 (\sin(2t\Omega) - 2t\Omega)}{8\Omega} \quad (3.111)$$

which, as we claimed, is divergent in the large  $t$  limit. If we do the  $\omega_2$  integration first, followed by  $\omega_1$  integration, for all the 8 terms in the original integrand (Eq. (3.92)), the sum of the extra terms (those corresponding to Eq. (3.111)) will vanish.

Eq. (3.111) corresponds to the extra term coming from the  $(n = 0, m = 1)$  term in the original integrand (Eq. (3.92)). The contribution from the corresponding  $(n = 0, m = -1)$  term will be exactly the same, while those from  $(n = \pm 1, m = 0)$  terms will be of the same magnitude but opposite sign, hence leading to cancellation. The remaining terms in Eq. (3.92) do not lead to any extra term.

### 3.4.5 TCL2/TCL4 for Ohmic Spectral Density with Drude cutoff

Next, we discuss the calculations for TCL2 and TCL4 generators ( $F^{(2)}$  and  $F^{(4)}$ , respectively) for Ohmic spectral density with Drude cutoff ( $J_D(\omega)$ , see Eq. (2.89)). As discussed in Sec. 2.2.1, the two-point correlation functions,  $\nu(t)$  and  $\eta(t)$  (Eq. (2.90) and Eq. (2.91)) can be exactly calculated for  $J_D(\omega)$ . Hence, these two-point correlation functions can be used directly to evaluate the time integrals of TCL2 and TCL4 coefficients (see Eq. (3.76)–Eq. (3.83), Eq. (3.30), and Eq. (3.31)) in the long time limit. This avoids the need to do

the double  $\omega$  integrals that were done in the case of our general results. The final result is then expressed in terms of a scalar, a single, or double infinite summation, which can be analytically evaluated in closed form or approximated numerically.

To simplify the calculations involved, we set  $a_3 = 0$  and  $a_1 = 1$  in the SBM Hamiltonian (Eq. (2.74)). Then the non-zero coefficients for the TCL2 generator are given as

$$F_{21}^{(2)} = \frac{2\gamma\Lambda\Omega}{\beta(\Lambda^2 + \Omega^2)} \left( 2\pi + \beta\Lambda \left[ -2\psi^{(0)} \left( \frac{\beta\Lambda}{2\pi} + 1 \right) + \psi^{(0)} \left( 1 - \frac{i\beta\Omega}{2\pi} \right) + \psi^{(0)} \left( \frac{i\beta\Omega}{2\pi} + 1 \right) \right] \right), \quad (3.112)$$

$$F_{22}^{(2)} = -\frac{2\pi\gamma\Lambda^2\Omega \coth\left(\frac{\beta\Omega}{2}\right)}{\Lambda^2 + \Omega^2}, \quad (3.113)$$

$$F_{30}^{(2)} = -\frac{2\pi\gamma\Lambda^2\Omega}{\Lambda^2 + \Omega^2}, \quad (3.114)$$

$$F_{33}^{(2)} = -\frac{2\pi\gamma\Lambda^2\Omega \coth\left(\frac{\beta\Omega}{2}\right)}{\Lambda^2 + \Omega^2}. \quad (3.115)$$

Here and in subsequent equations,  $\psi^{(0)}(x)$  and  $\psi^{(1)}(x)$  are the digamma and trigamma functions, respectively [111]. The TCL4 coefficients  $F_{33}^{(4)}$  and  $F_{30}^{(4)}$  can also be evaluated as

$$F_{30}^{(4)} = \frac{2\gamma^2\Lambda^3\Omega}{\beta(\Lambda^2 + \Omega^2)^3} \left\{ 4\pi\beta\Lambda(\Lambda^2 - 2\Omega^2)\psi^{(0)}\left(\frac{\beta\Lambda}{2\pi} + 1\right) + 8\pi^2\Omega^2 \right. \\ \left. - \beta\Lambda \left[ 2\pi(\Lambda^2 - i\Lambda\Omega - 2\Omega^2)\psi^{(0)}\left(1 - \frac{i\beta\Omega}{2\pi}\right) \right. \right. \\ \left. \left. + 2\pi(\Lambda^2 + i\Lambda\Omega - 2\Omega^2)\psi^{(0)}\left(\frac{i\beta\Omega}{2\pi} + 1\right) \right. \right. \\ \left. \left. - i\beta\Omega(\Lambda^2 + \Omega^2) \left( \psi^{(1)}\left(1 - \frac{i\beta\Omega}{2\pi}\right) - \psi^{(1)}\left(\frac{i\beta\Omega}{2\pi} + 1\right) \right) \right] \right\}, \quad (3.116)$$

$$\begin{aligned}
F_{33}^{(4)} = & \frac{\gamma^2 \Lambda^3 \Omega}{\pi \beta^2 (\Lambda^2 + \Omega^2)^3} \left\{ -2i\pi \beta^2 \Lambda (\Lambda^2 - 3\Omega^2) \psi^{(0)} \left( -\frac{i\beta\Omega}{2\pi} \right)^2 \right. \\
& + 2i\pi \beta^2 \Lambda (\Lambda^2 - 3\Omega^2) \psi^{(0)} \left( \frac{i\beta\Omega}{2\pi} \right)^2 + 32\pi^3 \Omega \\
& + 2\beta \psi^{(0)} \left( -\frac{i\beta\Omega}{2\pi} \right) \left( 2i\pi^2 (\Lambda + i\Omega)(\Lambda + 3i\Omega) - \beta^2 \Lambda \Omega (\Lambda^2 + \Omega^2) \right) \psi^{(1)} \left( -\frac{i\beta\Omega}{2\pi} \right) \\
& - 2i\pi \beta^2 (\Lambda - i\Omega)(\Lambda + i\Omega) \left( (\Lambda + i\Omega) \psi^{(1)} \left( -\frac{i\beta\Omega}{2\pi} \right) - (\Lambda - i\Omega) \psi^{(1)} \left( \frac{i\beta\Omega}{2\pi} \right) \right) \\
& + 2\beta \psi^{(0)} \left( \frac{i\beta\Omega}{2\pi} \right) \left( -\Lambda \beta^2 \Omega (\Lambda^2 + \Omega^2) \right) \psi^{(1)} \left( \frac{i\beta\Omega}{2\pi} \right) - 2i\pi^2 (\Lambda - i\Omega)(\Lambda - 3i\Omega) \\
& \left. - 2\pi^2 \beta^2 \Lambda \psi^{(0)} \left( \frac{\beta\Lambda}{2\pi} \right) \left[ \operatorname{csch}^2 \left( \frac{\beta\Omega}{2} \right) \left( \beta\Omega (\Lambda^2 + \Omega^2) - (\Lambda^2 - 3\Omega^2) \sinh(\beta\Omega) \right) \right] \right\}.
\end{aligned} \tag{3.117}$$

We are also able to calculate the TCL2 and TCL4 matrix elements for the general SBM (for  $a_3 \neq 0$ ), but are unable to easily reduce one of the infinite sums for  $F_{33}^{(4)}$  in closed analytical form. However, we are able to approximately do the summation numerically and show its consistency with our main results, which we discuss in detail in Sec. 4.3.1.

# Chapter 4

## Applications and Benchmarking

With the full asymptotic TCL4 generator  $F^{(4)}$  at hand, we can now investigate the temporal dynamics of the SBM beyond the TCL2 approximation by solving

$$\frac{d}{dt}\tilde{v}(t) = (F^{(0)} + \lambda^2 F^{(2)} + \lambda^4 F^{(4)})\tilde{v}(t). \quad (4.1)$$

In this chapter, we study some physical applications of the TCL4 generator. This includes studying the corrections to the dynamics of a DQD system, which, in some limit, can be approximated as a Spin-Boson model (see Sec. 4.1). We also study the corrections to the non-Markovianity of the TCL2 dynamics, coming from the TCL4 terms (see Sec. 4.2). We then benchmark our analytical calculations against HEOM and also against exact calculations tailored for the Ohmic spectral density with Drude cutoff (see Sec. 4.3).

### 4.1 Application to the Double-Quantum-Dot System

In this section, we use this TCL4-ME to study the dynamics of a semiconductor DQD system, which can be effectively modeled by the SBM as discussed in detail in Sec. 2.2.2 (see also [1]). The SBM parameters are related to the DQD physical parameters (detuning

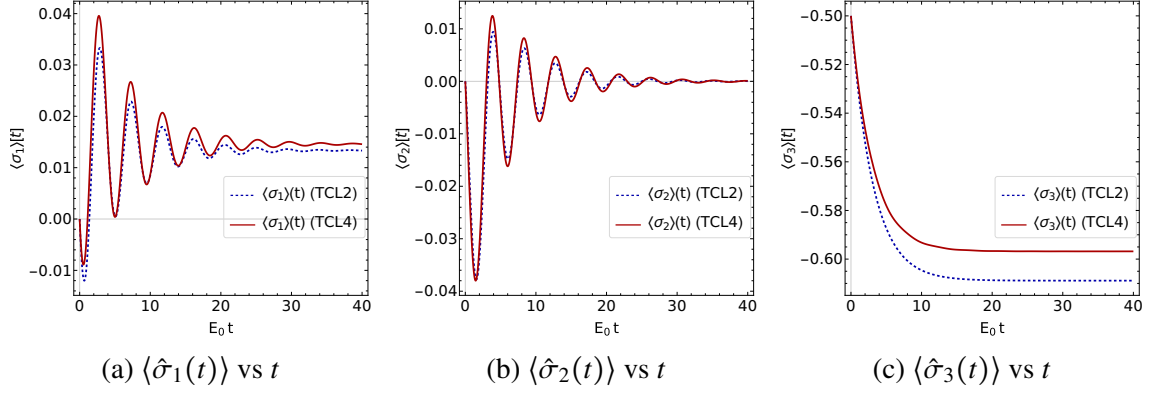


Figure 4.1: Time dynamics of the expectation value of (a)  $\langle \hat{\sigma}_1(t) \rangle$ , (b)  $\langle \hat{\sigma}_2(t) \rangle$ , and (c)  $\langle \hat{\sigma}_3(t) \rangle$  for a double quantum dot (DQD) system using second- and fourth-order master equations (TCL2: blue dotted lines and TCL4: red lines). This figure demonstrates how fourth-order corrections may become relevant in the dynamics of some dissipative systems, especially in the asymptotic limit for the populations (c), where TCL4 is needed to predict corrections to the Gibbs state population (see Sec. 2.1.2). The DQD model parameters are: detuning  $\epsilon = 1$ , inter-dot tunneling  $t_c = 0.5$ , system-environment coupling strength  $\gamma\lambda^2 = 0.4$ , inverse temperature  $\beta = 1$ , environmental cutoff frequency  $\omega_{\max} = 1$  and  $\omega_c = 1$ .  $\omega_c = c_s/d$ , where  $c_s$  is the speed of sound in the substrate and  $d$  is the inter-dot distance (see Eq. (2.99)). The initial values of the expectation values of these operators are chosen to be  $\langle \hat{\sigma}_1 \rangle = 0$ ,  $\langle \hat{\sigma}_2 \rangle = 0$ , and  $\langle \hat{\sigma}_3 \rangle = -0.5$ .

$\epsilon$  and inter-dot tunneling  $t_c$ ) as  $a_1 = \frac{2t_c}{\Omega}$ ,  $a_3 = \frac{\epsilon}{\Omega}$ ,  $\Omega^2 = \epsilon^2 + 4t_c^2$ . The spectral density is given as  $J(\omega) = \gamma\omega [1 - \text{sinc}(\omega/\omega_c)] \exp\{-\omega^2/(2\omega_{\max}^2)\}$ , where, we have  $\text{sinc}(x) \equiv \sin(x)/x$ . This spectral density effectively describes the bulk acoustic phonons in Gallium Arsenide (GaAs) DQDs [1, 41, 42, 44]. The parameter  $\omega_{\max}$  serves as the upper cut-off frequency, while  $\omega_c = c_s/d$ , where  $c_s$  is the speed of sound in the substrate and  $d$  is the inter-dot distance. Also, we note that since this spectral density (Eq. (2.99)) happens to fall under the class of spectral density assumed by us (Sec. 3.3.1), our TCL4 results are directly applicable here.

Fig. 4.1 plots the dynamics of a DQD system over time using TCL2 and TCL4. Fig. 4.1a, Fig. 4.1b and Fig. 4.1c show corrections to  $\langle \hat{\sigma}_1(t) \rangle$ ,  $\langle \hat{\sigma}_2(t) \rangle$  and  $\langle \hat{\sigma}_3(t) \rangle$  dynamics, respectively, for the initial state given as:  $\langle \hat{\sigma}_1(0) \rangle = 0$ ,  $\langle \hat{\sigma}_2(0) \rangle = 0$ , and  $\langle \hat{\sigma}_3(0) \rangle = -0.5$ . The remaining model parameters are chosen to be:  $\epsilon = 1$ ,  $t_c = 0.5$ ,  $\gamma\lambda^2 = 0.4$ ,  $\beta = 1$ ,  $\omega_{\max} = 1$  and  $\omega_c = 1$ .

We note that the 4th order correction to the SS value of  $\langle \hat{\sigma}_2(t) \rangle$  is zero, while the same is not true for the corresponding value of  $\langle \hat{\sigma}_1(t) \rangle$ . This is because for the present choice of the SBM model, the SS value of  $\langle \hat{\sigma}_2(t) \rangle$  is zero at all orders in the perturbation theory, as noted in Sec. 3.4.1. We conclude that TCL4 (compared to TCL2) provides corrections to the dynamics and SS of the DQD system that can become relevant in certain experimental conditions.

To get an estimate of the experimental regime where fourth- or even higher-order corrections will become important, we note that the norm ratio  $\|F^{(4)}\|_2/\|F^{(2)}\|_2 \approx 0.2$ . Since we have taken  $\gamma\lambda^2 = 0.4$ , this further reduces the relative size of the TCL4 generator as compared with the TCL2 generator to approximately 0.08. Since this is much smaller than 1, it supports the applicability of TCL4-ME in this parameter regime. On the other hand,  $\gamma\lambda^2 \approx 5$  would give the TCL4 and TCL2 terms of the same order, indicating either the need for higher-order corrections or the breakdown of the perturbative approach itself.

## 4.2 Non-Markovian Effects with TCL4

In this section, we quantify the non-Markovianity of the TCL2 and TCL4 dynamics of the SBM using the BLP measure (as discussed in Sec. 2.3.3; See also [50, 97]) for Ohmic spectral density with Drude cutoff ( $J_D(\omega) = \gamma\Lambda^2\omega/(\Lambda^2 + \omega^2)$ , see Eq. (2.89)). Here,  $\gamma$  is the coupling constant and  $\Lambda$  is the environment cutoff frequency. Here, we calculate the BLP measure ( $\mathcal{N}(\Phi)$ , see Eq. (2.143)) for different choices of temperature  $T$  and cutoff parameter  $\Lambda$  for the SBM [50].

We note that the BLP measure was originally derived for CPTP maps. The time-dependent TCL2n has error and hence non-CPness up to  $O(\lambda^{2n+2})$  and is also not guaranteed to be CP-divisible. Furthermore, for *time-independent* generators, the relevant diagnostic for the non-CPness is the negativity of the Kossakowski matrix [112]. And the Kossakowski matrix for TCL2 is known to have negative eigenvalues, which will be  $O(\lambda^2)$ , which can-

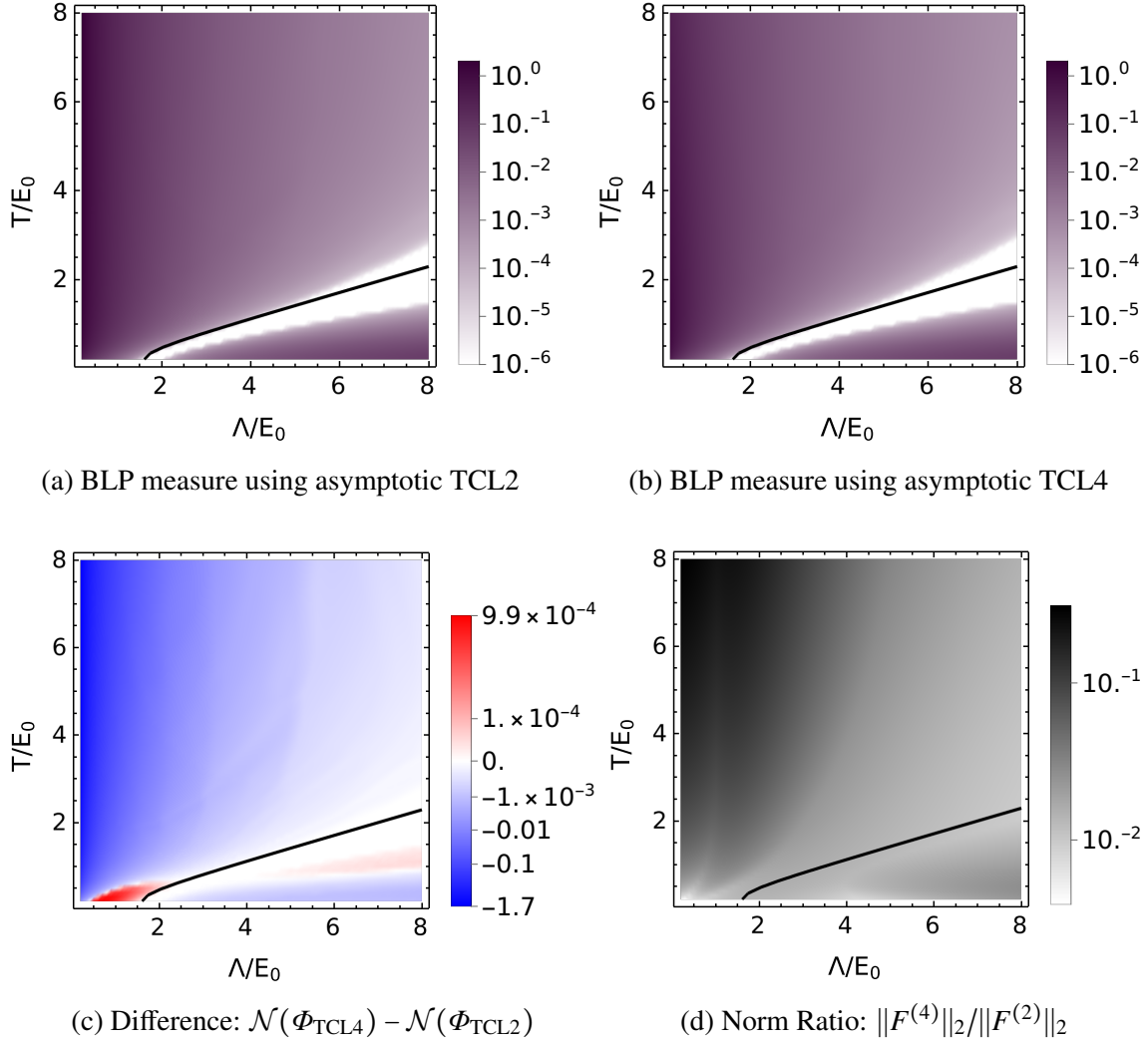


Figure 4.2: These figures plot the BLP measure,  $\mathcal{N}(\Phi)$  (see Eq. (2.143)), as logarithmic color plots calculated using (a) asymptotic TCL2 and (b) asymptotic TCL4 as a function of cutoff frequency  $\Lambda$  (see Eq. (2.89)) and temperature  $T$  for values of these parameters varying from 0.2 to 8. Part (c) plots the difference between these two quantities ( $\mathcal{N}(\Phi_{\text{TCL4}}) - \mathcal{N}(\Phi_{\text{TCL2}})$ ). (d) plots the  $L_2$  norm ratio of the TCL4 and TCL2 generators. The black line denotes the Markovian regime dictated by the resonance condition (see Eq. (4.2)). The maximization of the BLP measure was performed over 400 antipodal state pairs uniformly chosen over the surface of the Bloch sphere. The system frequency is  $\Omega = 1.6$  (see Eq. (2.72)), the coupling parameter is  $\gamma = 0.01$  (see Eq. (2.89)), and the bias is  $\theta = \frac{\pi}{2}$  (see the end of Sec. 2.2). (c) demonstrates that TCL2 can also overestimate the non-Markovianity, in the majority of the parameter regime in the present case. (d) shows the parameter regime of validity of TCL4, also indicating its failure in the high-temperature regime.

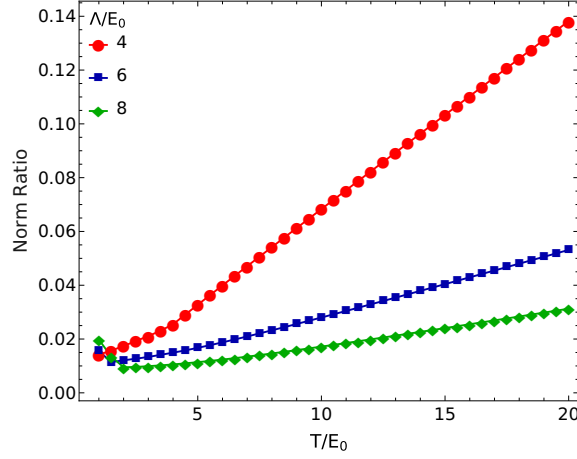


Figure 4.3: Plot of the  $L_2$  norm ratio for the TCL4 and TCL2 generators,  $\|F^{(4)}\|_2/\|F^{(2)}\|_2$  (see Eq. (2.102)), as a function of temperature for Ohmic spectral density with Drude cutoff for different values of cutoff frequency  $\Lambda$  (see Eq. (2.89)). All other model parameters are the same as in Fig. 4.2. For TCL4 to be valid, the norm ratio needs to be small. This figure shows a linear growth of the norm ratio as a function of  $T$ , as expected from the discussion in Sec. 4.2.

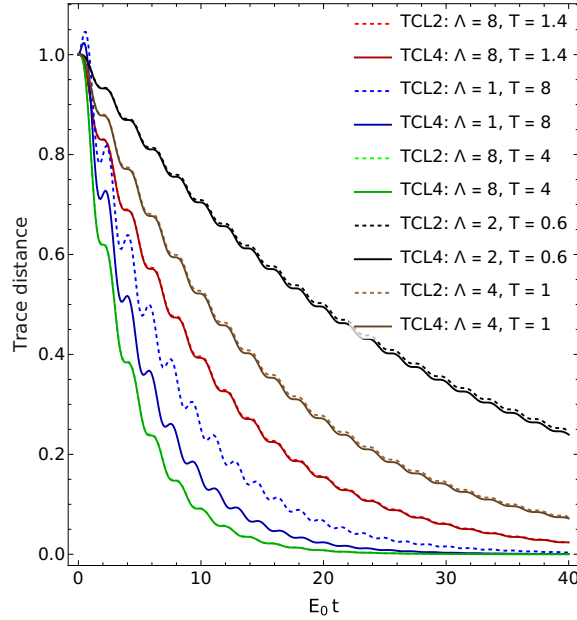


Figure 4.4: The trace distance between two states (given as  $\vec{v}_1(0) = (1, 1, 0, 0)$  and  $\vec{v}_2(0) = (1, -1, 0, 0)$  in Bloch vectorized form (Eq. (2.100))) is plotted as a function of time for the TCL2 and TCL4 master equations. All the model parameters in this figure are the same as those in Fig. 4.2. This plot demonstrates how, in the high- $T$  regime ( $T = 8$ ), TCL4 tends to speed up the equilibration, suppressing the revival.

not be removed by higher-order corrections. This means that the asymptotic TCL2n ME is not constrained to be CP even in the  $n \rightarrow \infty$  limit [113]. But this is consistent with the fact that the time-dependent TCL2n-ME is not CP-divisible.

Although the asymptotic TCL2n ME is non-CP, still we restrict the original motivation of the BLP measure to late-time information backflow [50]. To achieve this, we allow the states to evolve for a time  $\tau$  which is larger than the environment timescales  $\tau_B$  (given as  $\Lambda^{-1}$  and  $\beta/(2\pi)$ ) before starting the calculations for the BLP measure (Eq. (2.143)). This effectively restricts the initial states to a subset. Here, we choose  $\tau = 5 \max(\Lambda^{-1}, \beta/(2\pi))$ .

Fig. 4.2a and Fig. 4.2b plot the value of  $\mathcal{N}(\Phi)$  as logarithmic color plot for asymptotic TCL2 and TCL4, respectively, for the values of  $\Lambda$  and  $T$  ranging from 0.2 to 8 each. The remaining model parameters in this figure are fixed as:  $\Omega = 1.6$ ,  $\gamma = 0.01$ , and  $\theta = \frac{\pi}{2}$ .

As noted by Clos et al. [50], smaller values of  $T$  and  $\Lambda$  correspond to non-Markovian dynamics, except around the region given by the curve

$$\Lambda(T) = \Omega \sqrt{\frac{T \sinh\left(\frac{\Omega}{T}\right) + \Omega}{T \sinh\left(\frac{\Omega}{T}\right) - \Omega}}, \quad (4.2)$$

where resonance condition between the system and environment gives rise to a Markovian regime. This Markovian regime shows up as the white region in Figs. 4.2a and 4.2b.

This resonance condition can be understood when we consider the calculation of the TCL2 generator for Ohmic spectral density with Drude cutoff [50]. That is, when we replace the two point correlation function (Eq. (3.23)) in the frequency integral for the TCL2 generator (Eq. (3.19)), most of the contribution of the integral comes from the region around  $\omega = \Omega$  corresponding to the resonance condition. If the corresponding effective spectral density,  $f(\omega)$  happens to have maxima around this region, the system ‘sees’ effectively a flat environmental spectral density, giving rise to Markovian dynamics.

The mathematical condition for this is given by

$$\left. \frac{\partial}{\partial \omega} [J_D(\omega) \coth(\beta\omega/2)] \right|_{\omega=\Omega} = 0, \quad (4.3)$$

which gives rise to Eq. (4.2).

For each data point in Figs. 4.2a and 4.2b, the maximization in the BLP measure (Eq. (2.143)) was carried over 400 sets of antipodal state pairs chosen uniformly from the surface of the Bloch sphere. As discussed in Sec. 2.3.3, since the TCL2n-ME is a linear map, the antipodal points are optimal for the evaluation of the BLP measure [98]. See Sec. 4.4.1 for further technical details and discussions.

Fig. 4.2c plots the difference between these two plots ( $\mathcal{N}(\Phi_{TCL4}) - \mathcal{N}(\Phi_{TCL2})$ ) for the same range of  $\Lambda$  and  $T$ . The blue region in Fig. 4.2c, which spans the majority of the parameter space considered in the figure, indicates that TCL2-ME *overestimates* the non-Markovianity, as compared with TCL4-ME (and hence the exact result, since we are in a perturbatively weak coupling regime at non-zero temperature with two-point correlation functions that asymptotically decay exponentially with time [13]). On the other hand, we can also see regions, marked as red, where TCL2 *underestimates* the non-Markovianity, as compared with the exact result, by a much smaller magnitude.

Fig. 4.2d plots the  $L_2$  norm ratio of the TCL4 and TCL2 generator ( $\|F^{(4)}\|_2 / \|F^{(2)}\|_2$ ) over the same range of  $\Lambda$  and  $T$ .  $\|F^{(4)}\|_2 \ll \|F^{(2)}\|_2$  indicates the regime of validity of the TCL4-ME. We note how TCL4 has become more significant in the low  $\Lambda$  and low  $T$  limit. This is expected since the macroscopic derivation of the BR-ME (equivalently TCL2-ME) requires the assumption that  $\tau_R$ , the system relaxation time, is much larger than  $\tau_B$ , the environment timescale, governed by  $\Lambda^{-1}$  and  $\beta/(2\pi)$ . Hence, low  $\Lambda$  and  $T$  are expected to lead to the breakdown of TCL2, hence requiring larger corrections from TCL4.

As noted by Chen et al. [13], TCL4 also starts dominating in the large  $T$  limit, resulting

from the larger contribution from the  $\coth(\beta\omega/2)$  term. We can also see this in Fig. 4.3, which plots the  $L_2$  norm ratio for the TCL4 and TCL2 generators ( $\|F^{(4)}\|_2/\|F^{(2)}\|_2$ ) as a function of temperature for Ohmic spectral density with Drude cutoff for different values of cutoff  $\Lambda$ . All other model parameters are the same as in Fig. 4.2.

We note that for  $T \gg \Lambda$ , the norm ratio curve rises linearly. We have confirmed this behavior for different values of  $\Lambda$  as well as for the spectral density we used for the DQD system (see Eq. (2.99)). We note that this behavior can be explained for an arbitrary spectral density with some cutoff. As noted by Chen et al. [13], such divergence at high  $T$  is the result of the dominance of the  $\coth(\beta\omega/2)$  terms. We note that for  $\omega \ll T$ ,  $\coth(\beta\omega/2) \approx 2T/\omega$ . The dominant contribution to the TCL2n integral comes from the region  $\omega \leq \Lambda$ . When  $T \gg \Lambda$ , in this region, each factor of  $\coth(\beta\omega/2)$  can hence be approximated as  $2T/\omega$ . Since TCL2n integral has terms with a factor of  $\coth(\beta\omega/2)^n$ , in the large- $T$  limit, this dominating region will cause  $\|F^{(2n)}\|_2 \propto T^n$ . This explains the linear behavior of the norm ratio in the  $T \gg \Lambda$  region. We note that this argument does not require the frequency cutoff to be of Drude type. Hence, this argument has quite a general applicability.

Fig. 4.4 plots the trace distance dynamics for initial vectorized states (Eq. (2.100)) given as  $\vec{v}_1(0) = (1, 1, 0, 0)$  and  $\vec{v}_2(0) = (1, -1, 0, 0)$  for different choices of  $\Lambda$  and  $T$ , where the other model parameters are kept the same as in Fig. 4.2. Note that the choice of  $\Lambda$  and  $T$  is such that it samples curves from the red, blue, and white regions in Fig. 4.2c. Studying the trace distance dynamics in these regions can help us understand their distribution within the parameter space.

The dark blue regions in Fig. 4.2c tend to exist in high non-Markovian regimes, where the correction from TCL4 is significant enough to cause a faster equilibration of the system (see  $(\Lambda = 1, T = 8)$  curves in Fig. 4.4), giving rise to faster decay and hence decreased revival of the distinguishability. Hence, the region near the white Markovian regime in Fig. 4.2c becomes a necessary but not sufficient condition for the existence of the red

region in this figure. Here, the TCL4 correction is not strong enough to significantly speed up the equilibration, yet can, in some parameter regimes, give rise to a positive but small contribution to the revival of distinguishability (for example, see  $(\Lambda = 8, T = 1.4)$  and  $(\Lambda = 2, T = 0.6)$  curves in Fig. 4.4). We can contrast this with the  $(\Lambda = 8, T = 4)$  curve in Fig. 4.4, where TCL4 does not significantly speed up the equilibration, yet TCL2 *overestimates* the non-Markovianity.

For completeness, in Fig. 4.4, we also provide the curves corresponding to the white Markovian region in Fig. 4.2c (the  $\Lambda = 4, T = 1$  curves). For this curve, the trace distance dynamics undergo monotonous decay for both TCL2 and TCL4.

We note that for the blue curves in Fig. 4.4 (corresponding to  $\Lambda = 1, T = 8$ ), the trace distance between two states briefly and slightly rises above one for both TCL2 and TCL4, indicating positivity violation. Such positivity violation is expected for a perturbative master equation. We can check whether this positivity violation is unreasonably large by checking whether we are within the parameter regime for the validity of TCL4 (i.e., by comparing the  $L_2$  norm ratio of the TCL4 and TCL2 generator (the ratio of the highest singular values of these matrices), as given in Fig. 4.2d, which should be much smaller than 1). We can also check how the positivity violation scales as a function of  $\gamma$  to infer if it is reasonable. To do this, we define the magnitude of the positivity violation as

$$N(\gamma) = \int_0^{t_0} dt (|E_1(t)| + |E_2(t)| - 1), \quad (4.4)$$

where  $E_1(t)$  and  $E_2(t)$  are the instantaneous eigenvalues of the time evolved state and  $t_0 \gg \tau_R$ , where  $\tau_R$  is the relaxation timescale of the system. Fig. 4.5 plots  $N(\gamma)$  as a function of  $\gamma$  for the asymptotic TCL2 and TCL4 dynamics. Here, the initial state was chosen to be  $\vec{v}(0) = (1, 1, 0, 0)$  and  $\Lambda = 1, T = 8$  and  $\Omega = 1.6$  (corresponding to the blue curves in Fig. 4.4). Here, we have  $t_0 = 50$ , which, from Fig. 4.4, can be seen to be sufficiently large to allow the system to equilibrate.

We note that in Fig. 4.5, the curve corresponding to TCL2 is roughly linear in  $\gamma$ , which is expected because asymptotic TCL2 can give rise to positivity violation up to  $O(\gamma)$ . At lower values of  $\gamma$ , the TCL4 curve tends to agree with the TCL2 result. At higher values of  $\gamma$ , the fourth-order correction to TCL2 becomes dominant, which, in this case, leads to a reduction in the negativity. For the value of  $\gamma$  plotted, since the overall positivity violation is still less than  $O(\gamma)$ , we conclude that such a violation is not unreasonably large. For even higher values of  $\gamma$  not shown in this figure, the TCL4 dynamics become unstable and divergent and give rise to unreasonably large positivity violations.

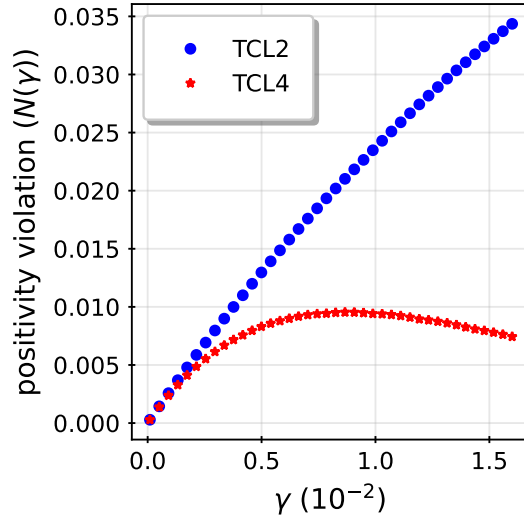


Figure 4.5: Plot for the total positivity violation,  $N(\gamma)$  (see Eq. (4.4)), as a function of the SE coupling strength  $\gamma$ . Here, the initial state was chosen to be  $\vec{v}(0) = (1, 1, 0, 0)$  and  $\Lambda = 1$ ,  $T = 8$  and  $\Omega = 1.6$  (corresponding to the blue curves in Fig. 4.4). This plot demonstrates that the positivity violation is linear in  $\gamma$  for both TCL2 and TCL4 in the small- $\gamma$  limit, which is expected and indicates that the positivity violation observed in this regime is reasonable.

Although the asymptotic TCL generators are time-independent, writing them in GKSL-like form generally introduces negative decay rates up to  $O(\lambda^2)$ . This makes the master equation non-CP and allows memory effects. These effects are visible in Fig. 4.2 and Fig. 4.4. Moreover, at the lower end of the temperature range, we find that TCL4 even enhances these memory effects (i.e., in the two disconnected red regions in Fig. 4.2c, near  $\Lambda \approx 0$ ,  $T \approx 0$  and large  $\Lambda$ ,  $T \approx 1$ , respectively). This is an example of late-time onset of

non-Markovian dynamics, with a higher-order TCL generator enhancing this effect in the low-temperature regime.

This result should be seen within the context of existing literature on late-time onset of non-Markovianity (see Peres [114] and related works). For example, Peres [114] discusses the late-time memory effect emerging from the long algebraic tail in the memory kernel equation for the decay of an unstable state. On a similar note, as discussed in Sec. 3.3.2, Lampert et al. [12] have recently reported that for algebraically decaying correlations, the asymptotic generator does not exist for  $\text{TCL}2n$  for  $n > n_{\text{max}}$  for some finite  $n_{\text{max}}$ . This indicates a breakdown of the perturbative master equation description at large times, giving rise to another type of late-time memory effect, possibly again originating from the long algebraic tail in the correlation function.

We note that Saurez et al. [115] have previously reported how the cumulant and Bloch Redfield ME tend to overestimate and underestimate the non-Markovianity, respectively, as compared with the numerically exact result given by HEOM.

## 4.3 Numerical Verification and Benchmarking

In this section, we perform 2 types of numerical verifications and benchmarking of our results:

1. Consistency checks against TCL4 calculations done for a specific spectral density.
2. Benchmarking against the numerically exact HEOM method.

### 4.3.1 Consistency for Ohmic spectral density with Drude Cutoff

As discussed in Sec. 2.2.2, for an Ohmic spectral density with Drude cutoff (see Eq. (2.89)), closed-form expressions for the two-point correlation functions  $\nu(t)$  and  $\eta(t)$  can be ex-

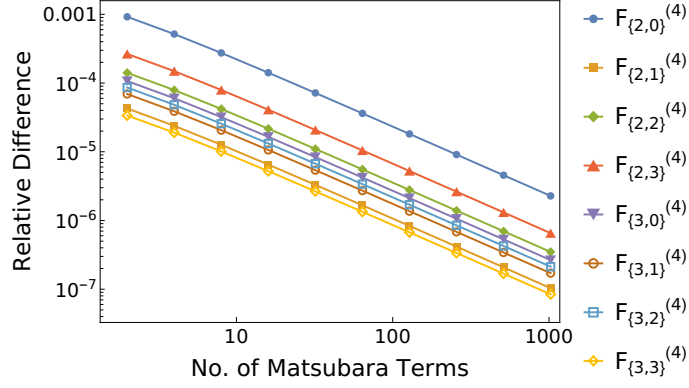


Figure 4.6: Relative difference between matrix elements of the asymptotic TCL4 generator,  $F^{(4)}$  (see Eq. (2.102)) for Ohmic spectral density with Drude cutoff, calculated using our general result and specialized calculations done specifically for the current choice of the spectral density, as a function of the number of Matsubara terms (see Eq. (2.91)) considered in the latter calculation. All free parameters of the model were randomly chosen (in weak coupling limit) and are specifically given as: coupling parameter  $\gamma = 3.58 \times 10^{-3}$ , environmental cutoff frequency  $\Lambda = 2.07 \times 10^{-1}$  (see Eq. (2.89)), system frequency  $\Omega = 1.91 \times 10^{-1}$  (see Eq. (2.72)), inverse temperature  $\beta = 3.15 \times 10^{-1}$  and bias angle  $\theta = 1.83 \times 10^{-1}$  (see the end of Sec. 2.2). Note that both the  $x$  and  $y$  axes on this plot are in log scale. This plot shows that the Drude results approach our exact calculations as  $1/N^m$ , where  $N$  is the number of Matsubara terms and  $m \approx 1$  as suggested by this plot.

pressed as  $\eta_D(t) = -\frac{\pi}{2}\gamma\Lambda^2 e^{-\Lambda t}$  and  $\nu_D(t) = \sum_{n=-\infty}^{\infty} \frac{\pi\gamma\Lambda^2(\Lambda e^{-\Lambda t} - |\mu_n|e^{-|\mu_n|t})}{\beta(\Lambda^2 - |\mu_n|^2)}$  where  $\mu_n = 2\pi n/\beta$  are Matsubara frequencies. (see Eqs. (2.90) and (2.91)).

Consequently, these closed-form expressions can be substituted directly into the time-domain integrals that define the TCL2 and TCL4 coefficients (see Eq. (3.30)) and evaluated in the long-time limit. This procedure circumvents the double  $\omega$ -integrals that were necessary in the more general treatment. The final result is symbolically expressed as

$$X_{ij}(N) = d_{ij} + \sum_{n=1}^N d'_{ij}(n) + \sum_{n,m=1}^N d''_{ij}(n,m) \quad (4.5)$$

$$F_{Dij}^{(4)} = \lim_{N \rightarrow \infty} X_{ij}(N) \quad (4.6)$$

Here,  $F_{Dij}^{(4)}$  is the corresponding TCL4 generator for  $J(\omega) = J_D(\omega)$  (Eq. (2.89)). This means that the final expression can be written as a sum over a constant term ( $d$ ) and a single and double infinite summation over functions  $d'(n)$  and  $d''(n,m)$ , respectively.

Although we calculated the expression of  $d$ ,  $d'(n)$  and  $d''(n, m)$  for all the TCL4 coefficients  $F_{Dij}^{(4)}$ , we are not able to do these infinite summations in closed form for all the values of  $\{i, j\}$  [52]. Instead, we numerically do this summation for a large and finite  $N$  to verify our general results.

In Fig. 4.6, we plot the relative difference, defined as

$$E_{\text{rel}}(N) \equiv (F'_{ij}^{(4)} - X_{ij}(N))/F'_{ij}^{(4)}, \quad (4.7)$$

as a function of  $N$ . Here  $F'_{ij}^{(4)}$  represents the numerical value of the TCL4 generator, obtained from our general results, for  $J(\omega) = J_D(\omega)$ . The free parameters of the model were chosen randomly (in weak coupling limit) to be:  $\gamma = 3.58 \times 10^{-3}$ ,  $\Lambda = 2.07 \times 10^{-1}$ ,  $\Omega = 1.91 \times 10^{-1}$ ,  $\beta = 3.15 \times 10^{-1}$ ,  $\theta = 1.83 \times 10^{-1}$ . Note that both the  $x$  and  $y$  axes on this plot are in log scale, and the relative difference for all coefficient matrices decays linearly. For some positive coefficient  $m$ , this implies a  $1/N^m$  type of decay of the relative difference. Sec. 4.3.1 suggests that  $m \approx 1$ , which is the expected rate of convergence for the Drude cutoff. Hence, this figure numerically indicates that the relative difference between these two quantities is at least  $O(10^{-6})$  and decays quickly when more Matsubara terms are considered.

We note that we can analytically evaluate the infinite summations for  $F_{D3,0}^{(4)}$  and  $F_{D2,0}^{(4)}$ . The subsequent relative difference is found to be  $O(10^{-12})$  (and can be further brought down by using higher precision numerical integration used in the evaluation of our general result), providing further numerical support for the validity of our results [52].

### 4.3.2 Comparison with HEOM

Fig. 4.7 compares the dynamics predicted by TCL2 and TCL4-MEs with those obtained from HEOM for Ohmic spectral density with Drude cutoff (Eq. (2.89)). The comparison

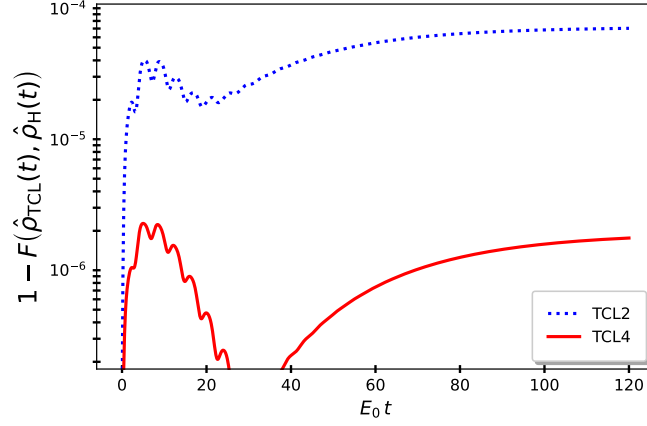


Figure 4.7: One minus the fidelity (see Eq. (4.8)) of the system state evolved by HEOM (Sec. 2.4) and the TCL master equation (the blue dotted line represents TCL2 and the red line represents TCL4). Calculations are for an SBM with an Ohmic spectral density with Drude cutoff and with the model parameters given as: system-environment coupling strength  $\gamma\lambda^2 = 0.02$  (see Eq. (2.89)), environmental cutoff frequency  $\Lambda = 1$  (see Eq. (2.89)), system frequency  $\Omega = 1.6$  (see Eq. (2.72)), inverse temperature  $\beta = 1$ , and bias angle  $\theta = 0.785$  (see the end of Sec. 2.2). For HEOM calculations, 32 Matsubara terms (see Eq. (2.91)) and 2 levels of hierarchy were retained. We note that the TCL4 dynamics shows an order-of-magnitude improvement in fidelity with HEOM over TCL2.

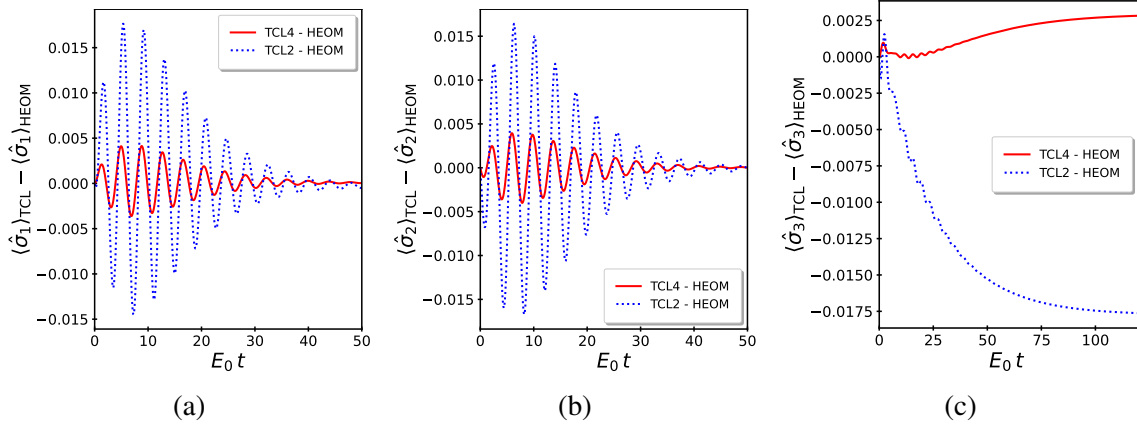


Figure 4.8: Difference between the TCL and HEOM Pauli matrix expectation values: (a)  $\langle \hat{\sigma}_1 \rangle$ , (b)  $\langle \hat{\sigma}_2 \rangle$  and (c)  $\langle \hat{\sigma}_3 \rangle$  (see Eq. (2.100)) as a function of time. All parameters are the same as in Fig. 4.7. This figure shows how the observable expectation values from TCL4 dynamics are closer to HEOM than those from TCL2.

is quantified by the fidelity, [96]

$$F(\hat{\rho}_{\text{TCL}}(t), \hat{\rho}_{\text{H}}(t)) = \text{Tr} \sqrt{\sqrt{\hat{\rho}_{\text{H}}(t)} \hat{\rho}_{\text{TCL}}(t) \sqrt{\hat{\rho}_{\text{H}}(t)}}, \quad (4.8)$$

between the system state evolved by the TCL ME ( $\hat{\rho}_{\text{TCL}}$ ) and the HEOM state ( $\hat{\rho}_{\text{H}}$ ). The model parameters in the figure are:  $\gamma\lambda^2 = 2. \times 10^{-2}$ ,  $\Lambda = 1$ ,  $\Omega = 1.6$ ,  $\beta = 1$ ,  $\theta = 7.85 \times 10^{-1}$ , while at the HEOM side, we retained 32 Matsubara terms (Eq. (2.90) and Eq. (2.91)) and 2 levels of hierarchies. We checked the robustness of the results in this plot by going to higher Matsubara terms and hierarchy depths (128 and 4, respectively). We note that closeness between the TCL4 and HEOM dynamics increases as we increase the precision of the HEOM calculations, while the same is not true for TCL2 dynamics.

Note that since our TCL4 result is applicable in the asymptotic limit ( $t \gg \tau_B$ ), the above calculations were performed in this same limit. That is, we initialized a state  $\hat{\sigma}(0) = |+\rangle\langle+|$ , then calculated a time  $\tau \gg \{\Lambda^{-1}, \beta/(2\pi)\}$ , (here,  $\tau = 5$ ), and then defined  $\hat{\rho}_{\text{H}}(t) \equiv \hat{\sigma}(t + \tau)$  and initialized the TCL state as  $\hat{\rho}_{\text{TCL}}(0) = \hat{\sigma}(\tau)$ .

For ease of visualization, Fig. 4.7 plots  $1 - F(\hat{\rho}_{\text{TCL}}(t), \hat{\rho}_{\text{H}}(t))$  for both TCL2 and TCL4. We conclude that TCL4-ME maintains a significantly higher fidelity with the HEOM results compared to TCL2-ME. Fig. 4.8 plots the difference between TCL and HEOM values of (a)  $\langle\hat{\sigma}_1\rangle$ , (b)  $\langle\hat{\sigma}_2\rangle$  and (c)  $\langle\hat{\sigma}_3\rangle$  as a function of time.

## 4.4 Technical Details

### 4.4.1 Parametrization on the Bloch sphere

In Fig. 4.2, to generate Bloch vectors that are uniformly distributed over the surface of the Bloch sphere, we use the following parametrisation. Let  $u, v \in [0, 1]$  be independent random variables drawn from a uniform distribution. The Cartesian component of the

corresponding Bloch vector is then given by:

$$\begin{aligned}x(u, v) &= \cos(2\pi u) \cdot \sin(\cos^{-1}(2v - 1)), \\y(u, v) &= \sin(2\pi u) \cdot \sin(\cos^{-1}(2v - 1)), \\z(v) &= \cos(\cos^{-1}(2v - 1)).\end{aligned}$$

This mapping ensures that the generated points are uniformly distributed over the sphere's surface.

To calculate the non-Markovianity measure  $\mathcal{N}(\Phi)$  in Fig. 4.2, we uniformly generate 20 values of variables  $u$  and  $v$ , each, from their respective domains, giving rise to a set of 400 states,  $[x(u, v), y(u, v), z(v)]$ , on the Bloch surface. For each such state, the corresponding antipodal state is chosen as its pair, and the corresponding BLP calculation is done as explained in Sec. 4.2. The trace distance between these antipodal state pairs is evolved until it decays close enough to zero, as can be seen in Fig. 4.4 for some of the curves. For numerical optimization, this time interval,  $t_{max}$ , for which the BLP integral (Eq. (2.143)) needs to be calculated, is determined for each value of  $\Lambda$  and  $T$ . For given values of  $\Lambda$  and  $T$ , let  $\hat{\rho}_{\Lambda, T}(0)$  be the state farthest away from the corresponding Gibbs state in terms of trace distance. Then  $t_{max}$  is determined as the smallest time such that for the trace distance, we have  $D(\hat{\rho}_{\Lambda, T}(t_{max}), \hat{\rho}_{eq}) < \epsilon$ , where  $\hat{\rho}_{\Lambda, T}(t_{max})$  is the initial state evolved under TCL2,  $\hat{\rho}_{eq}$  is the SS of TCL2 and  $\epsilon$  is a small threshold, chosen to be equal to 0.001. We note that the qualitative features in Fig. 4.2 were found to be robust under variation of  $\epsilon$  and other numerical precision parameters.

#### 4.4.2 How to use the Supplementary material

All the main results of this work are available in `TCL4DynamicsSpinBosonResults.nb` as part of the Supplementary Material [52].

## TCL-ME: General Derivation

- ‘TCL4OperatorFormDerivation.wl’ derives the reduced form of the TCL4 generator (Eq. (2.64)) starting from Eq. (2.62).
- ‘TCLIntegrandCalcs.wl’ starts from the expression of the TCL2 and TCL4 generators that can be found in [94], and derives the matrix elements of the TCL4 and TCL2 generator in Bloch vectorized format.
- ‘TCL2GeneratorCalc.wl’ uses these results to evaluate the general TCL2 generator.
- ‘TCL4TripleTimeIntegral.wl’ symbolically evaluates the triple time integrals of the TCL4 generator matrix elements.
- ‘TCL4OmegaIntegral.wl’ then evaluates the frequency integrals in the large time limit.

## Solving for dynamics

- ‘DQDTCL4GeneratorEvaluation.wl’ reproduces Fig. 4.1 and can also be used to solve dynamics for other spectral densities.
- ‘TCL4GeneratorEvaluationForDrude.wl’ performs similar calculations for the Ohmic spectral density with Drude cutoff.
- ‘02SSCalcSpinBoson.nb’ analytically evaluates the 2nd and 4th order SS results.

## Verification of our results

Verification scripts are organized as follows:

- ‘TCL4DrudeGeneratorCalc.wl’ performs the TCL4 calculations for Ohmic spectral density with Drude cutoff.
- ‘TCL2DrudeGeneratorCalc.wl’ performs the TCL2 calculations for Ohmic spectral density with Drude cutoff.
- ‘TCL4Verification.wl’ verifies our general result with these Drude calculations and reproduces Fig. 4.6.
- ‘TCL4HighPrecisionVerification.wl’ does the same verification at higher precision for  $F_{20}^{(4)}$  and  $F_{30}^{(4)}$ .

HEOM benchmarking uses ‘TCLVsHEOMFidelity.wl’ and ‘tcl\_vs\_heom.py’.

‘TCLVsHEOMFidelity.wl’ does the TCL-side calculations and dumps the results into ‘python\_objects.txt’. Then ‘tcl\_vs\_heom.py’ reads these results and runs the HEOM side calculations using the qutip python package, reproducing Fig. 4.7.

### Non-Markovianity Calculations

- ‘AntipodalTCL2NM.wl’ and ‘AntipodalTCL4NM.wl’ do the non-Markovianity calculations for antipodal states, while ‘AntipodalSBMProjectNMPlot.wl’ plots the results (Fig. 4.2).
- ‘GeneralTCL2NM.wl’ and ‘GeneralTCL4NM.wl’ do the non-Markovianity calculations for general states.
- ‘TraceDistanceDynamicsPlot.wl’ reproduces Fig. 4.4.

# Chapter 5

## Ultra-Strong-Coupling Mean-Force Gibbs States

### 5.1 Ultra-Strong Coupling Mean Force Gibbs State for Caldeira-Leggett model

Our goal is to rederive the USC-MFGS for the general CL model, originally derived in [22] using perturbation theory. Here, we will be using the path integral approach, with the aim to eventually generalize this result to a wider class of anharmonic environment models. We start from the path integral expression for the MFGS for a general CL model (derived in Eq. (2.156)) given as:

$$\rho_{\text{MFGS}}(a, b) = \tilde{Z}^{-1} \int_{\tilde{a}}^{\tilde{b}} \mathcal{D}A(t) \int_a^b \mathcal{D}\phi(t) e^{-S_S[A(t), \phi(t)]} I[A(t)]. \quad (5.1)$$

$$I_k[A(t)] = \int_{-\infty}^{\infty} dx \int_x^x \mathcal{D}q_k(t) e^{-S_k[q_k(t), A(t)]}. \quad (5.2)$$

$$S_k[q_k(t), A(t)] \equiv \int_0^\beta dt \left\{ \frac{m_k}{2} \dot{q}_k(t)^2 + \frac{m_k \omega_k^2}{2} (q_k(t) - \alpha_k A(t))^2 \right\}. \quad (5.3)$$

Let us choose an arbitrarily large but finite length scale  $\Delta$  such that whenever  $|q_k(t) -$

$|\alpha_k A(t)| > \Delta$  for any  $t$ , the potential energy (PE) cost of the corresponding path,  $q_k(t)$ , will be very high, and hence its contribution to the path integral will be negligible. We can hence write, for all paths  $q_k^*(t)$  that *do* have significant contribution to the path integral,

$$|q_k^*(t) - \alpha_k A(t)| < \Delta. \quad (5.4)$$

Let us define

$$\langle A \rangle \equiv \frac{1}{\beta} \int_0^\beta dt A(t), \quad (5.5)$$

$$\langle A^2 \rangle \equiv \frac{1}{\beta} \int_0^\beta dt A(t)^2, \quad (5.6)$$

$$\sigma_A^2 \equiv \langle A^2 \rangle - \langle A \rangle^2. \quad (5.7)$$

Then, in Proposition 5, we have proven that if  $\sigma_A^2 \gg \Delta^2/\alpha_k^2$ , then

$$\frac{1}{\beta} \int_0^\beta dt \dot{q}_k^*(t)^2 \geq \alpha_k^2 \mu \frac{\sigma_A^2}{\beta^2}. \quad (5.8)$$

Here  $\mu > 0$  is some constant. Now, note that in the USC limit, defined as

$$\lim c_k \rightarrow \infty, \quad (5.9)$$

we have  $\alpha_k \rightarrow \infty$  (Eq. (2.153)). In this limit, unless  $\sigma_A = O(\Delta/\alpha_k)$ , the RHS in Eq. (5.8) diverges. This causes the kinetic term  $\dot{q}_k^*(t)^2$  in the action  $S_k[q_k(t), A(t)]$  (Eq. (2.158)) to diverge. Therefore, in the USC limit (Eq. (5.9)), paths  $q_k^*(t)$  (which have been defined to have convergent PE cost) will have divergent kinetic energy cost unless  $\sigma_A$  vanishes. In other words, unless we have

$$A(t) = A(0) = \tilde{a}, \quad \text{for some constant } \tilde{a}. \quad (5.10)$$

As we will see, Eq. (5.10) will greatly simplify the evaluation of the MFGS path integral

(Eq. (2.156)). But before getting into that, we need to address a subtlety. If the system lives in a discrete Hilbert space, then  $A(t)$  may not be continuous and differentiable everywhere, leading to potential mathematical irregularities. Although the results and proofs in this paper only require the paths  $A(t)$  to be square integrable (and not continuous and differentiable), we note that these mathematical irregularities can be addressed by substituting  $A(t)$  with a continuous and differentiable function  $X(t)$  that closely approximates it, such that the induced error,  $|I_k[A(t)] - I_k[X(t)]|$ , is arbitrarily small. For instance, Fig. 5.1 illustrates how  $X(t)$ , using a cubic polynomial near  $t = 1$ , smoothly approximates  $A(t)$ 's discrete jump.

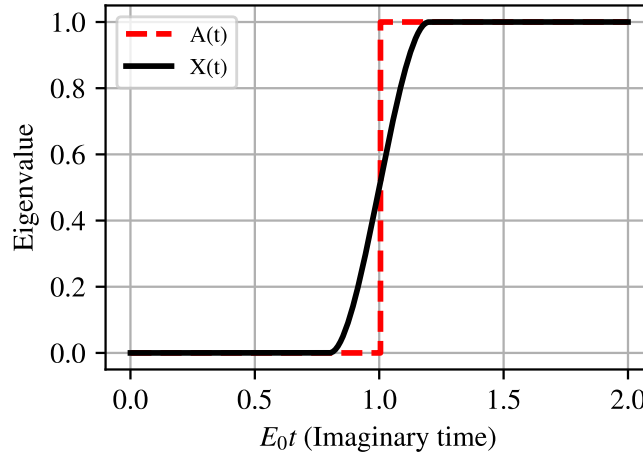


Figure 5.1: In the path integral approach, we approximate a piecewise constant function,  $A(t)$ , with a continuous and differentiable function  $X(t)$ . The function  $X(t)$  is equal to  $A(t)$  everywhere except near the discontinuous jump in  $A(t)$  (when  $1 - \delta < t < 1 + \delta$ , for  $\delta = 0.2$ ). Near  $t = 1$ ,  $X(t)$  takes the form of a cubic function,  $f(t') = a_0 + a_1 t' + a_3 t'^3$ , with  $t' = t - 1$ ,  $a_0 = 1/2$ ,  $a_1 = 3/(4\delta)$  and  $a_3 = -1/(4\delta^3)$ . This means that we have  $\lim_{\delta \rightarrow 0} X(t) = A(t)$ . This continuous approximation of a discrete jump is not necessary for the proof of the results, but can make the arguments intuitive.

Now, given Eq. (5.10), the expression for the influence functional (Eq. (2.157)) simplifies as

$$I_k[\tilde{a}] = \int_{-\infty}^{\infty} dx \int_x^x \mathcal{D}q_k(t) e^{-S_k[q_k(t), \tilde{a}]} \quad (5.11)$$

$$= \int_{-\infty}^{\infty} dx \int_{x-\alpha_k \tilde{a}}^{x-\alpha_k \tilde{a}} \mathcal{D}x_k(t) e^{-S_k[x_k(t), 0]} \quad (5.12)$$

$$= \int_{-\infty}^{\infty} dx \int_x^x \mathcal{D}x_k(t) e^{-S_k[x_k(t), 0]} \quad (5.13)$$

$$= I_k, \quad \text{which is independent of } \tilde{a}. \quad (5.14)$$

Here in Eq. (5.12), we defined  $x_k(t) \equiv q_k(t) - \alpha_k \tilde{a}$  and used the relation  $S_k[q_k(t), \tilde{a}] = S_k[x_k(t), 0]$  (Eq. (2.158)). We hence have that  $I_k[\tilde{a}] \equiv I_k$  is independent of  $\tilde{a}$ . Therefore, the only contribution of the environment side path integral is to eliminate all the system side paths that do not satisfy Eq. (5.10). This means that jumps within a degenerate subspace are still allowed and with equal weight as far as the environment side path integral is concerned. Hence, the full MFGS path integral (Eq. (2.156)) simplifies as

$$\rho_{\text{USC}}(a, b) = \tilde{Z}^{-1} I \int_a^b \mathcal{D}\phi(t) \exp \{ -S_S[\tilde{a}, \phi(t)] \}. \quad (5.15)$$

Here  $a$  and  $b$  are the eigenvalues of the operator  $\hat{\phi}$  and  $\tilde{a}$  is the eigenvalue of  $\hat{A}$ . [116] Then, the USC-MFGS is given as

$$\hat{\rho}_{\text{USC}} = Z^{-1} \exp \{ -\beta \tilde{H} \}, \quad (5.16)$$

$$\tilde{H} \equiv \sum_i \hat{P}_i \hat{H}_S \hat{P}_i. \quad (5.17)$$

Here  $\hat{P}_i$  is the projection operator on the  $i$ th eigensubspace of the system coupling-operator,  $\hat{A}$ , and  $Z$  is the normalization constant. Eq. (5.16) is equivalent to the USC-MFGS derived by Cresser and Anders using perturbation theory [22]. It also reduces to the USC-MFGS derived earlier for a CV system [81]. Note that the derivation provided in this section is applicable for a generic CL model, discrete or continuous. See Sec. 5.5.3 for more details.

## 5.2 Ultra-Strong Coupling Mean Force Gibbs State for Generalized Caldeira-Leggett model

The generalization of the CL model has been considered by several authors [70, 72–74, 77, 78] and can be characterized by an interaction Hamiltonian,  $\hat{H}_I$  (Eq. (2.152)), of the form

$$\hat{H}_I = \sum_k \left[ \frac{\hat{p}_k^2}{2m_k} + V_k(\hat{q}_k, c_k \hat{A}) \right]. \quad (5.18)$$

Let  $V_k(x, y)$  be some function over scalars. Then, let  $\hat{X}$  and  $\hat{Y}$  be some commuting hermitian operators defined as

$$\hat{X} = \sum_i x_i |i\rangle \langle i|, \quad (5.19)$$

$$\hat{Y} = \sum_i y_i |i\rangle \langle i|. \quad (5.20)$$

Then, we define  $V_k(\hat{X}, \hat{Y})$  as

$$V_k(\hat{X}, \hat{Y}) \equiv \sum_i V_k(x_i, y_i) |i\rangle \langle i|. \quad (5.21)$$

We note that  $\hat{q}_k$  and  $\hat{A}$  commute, so this definition is applicable to  $V_k(\hat{q}_k, c_k \hat{A})$ .

Next, we assume that  $V_k(x, y)$  is a potential function bounded from below with a constraint that it should not renormalize the free effective system Hamiltonian  $\hat{H}_S$ . [4, 70, 78, 117] This is usually ensured by adding a so-called counter term in the potential,  $V_k(x, y)$ , which compensates for the shift in  $\hat{H}_S$  because of the environment. Here, we assume that such a counter term has already been incorporated into  $V_k(x, y)$ , which translates into demanding that for a fixed value of  $y$ , if  $x = \tilde{x}_k(y)$  is the point at which  $V_k(x, y)$  has a global minimum,

then [4, 78]

$$V_k(\tilde{x}_k(y), y) = 0. \quad (5.22)$$

We again remark that all of this just amounts to a redefinition of the free Hamiltonian and the interaction Hamiltonian, and is not an assumption on the model.

These generalized CL models have been studied in various contexts. For instance, they have been used to explore the influence of an anharmonic environment on the non-Markovian dynamics of open systems [78], to investigate certain condensed phase processes such as electron-transfer reactions [72–74, 77], and to examine the electronic absorption spectra of chromophores embedded in condensed phase environments. [70]

Here, we will generalize the derivation for the USC-MFGS provided in Sec. 5.1 to such a larger class of model that we call the Generalized Caldeira-Leggett (GCL) model. In order to proceed with the derivation of the USC-MFGS for such systems, we make two more physically motivated assumptions on the form of the potential  $V_k(x, y)$  for our GCL model, i.e.,

$$\lim_{x \rightarrow \pm\infty} V_k(\tilde{x}_k(y) + x, y) = \Omega(|x|) \quad \forall y, \quad (5.23)$$

$$\frac{d}{dy} \tilde{x}_k(y) \geq \Omega_0, \quad (5.24)$$

where  $\Omega_0$  is some positive constant. In Eq. (5.23), we have used the big Omega notation [118] which, given two non-negative functions  $f(x)$  and  $g(x)$  such that

$$g(x) = \Omega(f(x)), \quad (5.25)$$

is defined to imply that there exists a positive number  $C$  such that

$$g(x) \geq Cf(x). \quad (5.26)$$

Also, here,  $\tilde{x}_k(y)$  is assumed to be continuous and differentiable everywhere. We remark

that the continuity of the function  $\tilde{x}(y)$  is not affected by whether the system in question lives in a discrete dimensional Hilbert space or not because here we are treating  $V_k(x, y)$  and  $\tilde{x}(y)$  as generic functions that can act on continuous variables as well as discrete operators.

Justification for Eq. (5.23) is that keeping the system variable,  $y$ , fixed, if we move the environment variable  $x$  far away from its global minima point  $\tilde{x}_k(y)$ , then the value of the potential rises at least linearly with  $|x - \tilde{x}_k(y)|$ . That is, we assume that the system and environment variables are attractively coupled to each other.

We can motivate the second assumption as following: since we can choose  $\Omega_0$  to be as small as we want, the alternative to this assumption could be that  $|d\tilde{x}_k(y)/dy| \approx 0$ , then this would mean that for a large variation in  $y$ ,  $\tilde{x}_k(y)$  would be almost constant (i.e.,  $\tilde{x}_k(y) \approx x_0$ ) and for the corresponding value of the potential, we will have  $V_k(x_0, y) \approx 0$  (Eq. (5.22)). Hence, the assumption Eq. (5.24) is applicable whenever the interaction potential is sensitive to a large change in the variable  $y$  while  $x$  is held constant.

The expression for the action,  $S_k[q_k(t), A(t)]$  (Eq. (2.157)) for the GCL model now becomes,

$$S_k[q_k(t), A(t)] = \int_0^\beta dt \left\{ \frac{m_k}{2} \dot{q}_k(t)^2 + V_k(q_k(t), c_k A(t)) \right\}. \quad (5.27)$$

Eq. (5.23) implies that, for a fixed value of  $y$ , there is a (perhaps) large but essentially finite basin with length scale  $\Delta$  about the position  $x = \tilde{x}_k(y)$ , such that all paths  $q_k(t)$  that explore the region  $|x - \tilde{x}_k(y)| > \Delta$  will have a PE cost so high that the contribution of these paths to the path integral will be negligible. Hence, for all paths  $q_k^*(t)$  that *do* have a significant contribution to the path integral, we again have that

$$|q_k^*(t) - \tilde{x}_k(c_k A(t))| < \Delta. \quad (5.28)$$

Since  $\tilde{x}(c_k A(t))$  is ultimately a function of  $t$ , we can define  $\langle \tilde{x}_A \rangle$ ,  $\langle \tilde{x}_A^2 \rangle$  and  $\sigma_{\tilde{x}_A}^2$  analogous to Eq. (5.5)-Eq. (5.7). Next, given Eq. (5.24), we prove in Proposition 6 that

$$\sigma_{\tilde{x}_A}^2 \geq \Omega_0^2 c_k^2 \sigma_A^2. \quad (5.29)$$

Next, we note that if  $\sigma_{\tilde{x}_A} \approx \Delta$ , then  $\sigma_A = (1/\Omega_0)O(\Delta/c_k)$ , which vanishes in the USC limit (Eq. (5.9)). Alternatively, if we instead assume that

$$\sigma_{\tilde{x}_A}^2 \gg \Delta^2, \quad (5.30)$$

then, using Eq. (5.28), in Proposition 5 we prove that

$$\frac{1}{\beta} \int_0^\beta dt \dot{q}_k^*(t)^2 \geq \mu \frac{\sigma_{\tilde{x}_A}^2}{\beta^2} \quad (5.31)$$

$$\geq \Omega_0^2 c_k^2 \mu \frac{\sigma_A^2}{\beta^2}, \quad \text{using Eq. (5.29).} \quad (5.32)$$

Here  $\mu > 0$ . We have already encountered an inequality similar to Eq. (5.32) in the context of the CL model (Eq. (5.8)). Again, we are led to a similar conclusion that in the USC limit (Eq. (5.9)), paths  $q_k^*(t)$  (which have been defined to have convergent PE cost) will have divergent kinetic energy cost unless  $\sigma_A$  vanishes. Therefore, again we have that  $A(t) = A(0) = \tilde{a}$ , for some constant  $\tilde{a}$  (Eq. (5.10)). The expression for the influence functional (Eq. (2.157)) hence simplifies as

$$I_k[\tilde{a}] = \int_{-\infty}^{\infty} dx \int_x^x \mathcal{D}q_k(t) e^{-S_k[q_k(t), \tilde{a}]} \quad (5.33)$$

$$\implies I[\tilde{a}] = \text{Tr} \left[ e^{-\beta \hat{H}_I(\tilde{a})} \right]. \quad (5.34)$$

Here, for a scalar  $z$ , we have defined

$$\hat{H}_I(z) \equiv \sum_k \left[ \hat{p}_k^2 / (2m_k) + V_k(\hat{q}_k, c_k z) \right]. \quad (5.35)$$

We note that the large  $c_k$  limit of  $V_k(\hat{q}_k, c_k z)$  has to be well defined above. The expression for the full MFGS path integral (Eq. (2.156)) then becomes

$$\rho_{\text{USC}}(a, b) = \tilde{Z}^{-1} I[\tilde{a}] \int_a^b \mathcal{D}\phi(t) \exp \{ -S_S[\tilde{a}, \phi(t)] \}. \quad (5.36)$$

Here  $a$  and  $b$  are eigenvalues of the operator  $\hat{\phi}$  and  $\tilde{a}$  is eigenvalue of  $\hat{A}$ . [116] The USC-MFGS for GCL model is then given as

$$\hat{\rho}_{\text{USC}} = Z^{-1} \exp \{ -\beta \tilde{H} \} \quad (5.37)$$

$$\tilde{H} \equiv \sum_i \hat{P}_i (\hat{H}_S + \hat{V}_0) \hat{P}_i. \quad (5.38)$$

Here  $Z$  is the normalization constant and  $\hat{P}_i$  is the projection operator on the  $i$ th degenerate subspace of the operator  $\hat{A}$  with eigenvalue  $A_i$ . Here,  $\hat{V}_0$  is defined as

$$\hat{V}_0 = \frac{-1}{\beta} \sum_i \log \left( \text{Tr} \left( e^{-\beta \hat{H}_I(A_i)} \right) \right) \hat{P}_i, \quad (5.39)$$

where  $\hat{H}_I(A_i)$  is as defined in Eq. (5.35).

The key takeaway here is that although the USC-MFGS for the GCL model is still diagonal in the basis of the system coupling-operator  $\hat{A}$ , the actual expression does deviate from the CL-USC result. Determining the actual expression for the GCL-USC result would involve calculating the Gibbs partition function corresponding to the free environment Hamiltonian,  $\hat{H}_I(A_i)$ , as a function of different values of  $A_i$ , and hence a closed form expression is not possible without further information on the form of  $\hat{H}_I(A_i)$ .

### 5.2.1 Special Case

Since the CL-USC result gets modified for the GCL case, we will now identify a subclass within the GCL model, which we will call the GCL2 model, for which the USC-MFGS result remains the same as that for the CL case, and hence can also be determined in

closed form. To this end, let us assume a special form of the GCL model potential  $V_k(x, y)$  (Eq. (5.18)) as

$$V_k(x, y) = U_k(x - y). \quad (5.40)$$

Generalization of the CL model of this form has been considered before in literature [72] and physically reflects a symmetry in the potential such that we have  $V_k(x + w, y + w) = V_k(x, y)$ . The function  $\tilde{x}_k(y)$ , defined earlier, can now be expressed as

$$\tilde{x}_k(y) = y + x_k, \quad (5.41)$$

where  $x_k$  is some constant. Note how  $d\tilde{x}_k(y)/dy = 1$  and hence the corresponding GCL model assumption (Eq. (5.24)) is automatically satisfied here. The requirement that  $U_k(x)$  does not renormalize the free system Hamiltonian (Eq. (5.22)), on the other hand, translates into

$$U_k(x_k) = 0. \quad (5.42)$$

Similarly, the final GCL model assumption (Eq. (5.23)) translates here as

$$\lim_{x \rightarrow \pm\infty} U_k(x_k + x) = \mathcal{O}(|x|). \quad (5.43)$$

The remaining argument goes as before. The modified environment side action (Eq. (5.27)),

$$S_k[q_k(t), A(t)] \equiv \int_0^\beta dt \left\{ \frac{m_k}{2} \dot{q}_k(t)^2 + U_k(q_k(t) - c_k A(t)) \right\}, \quad (5.44)$$

gives the following expression for the influence functional, analogous to Eq. (5.33),

$$I_k[\tilde{a}] = \int_{-\infty}^{\infty} dx \int_x^x \mathcal{D}q_k(t) e^{-S_k[q_k(t), \tilde{a}]} \quad (5.45)$$

$$= \int_{-\infty}^{\infty} dx \int_{x-c_k\tilde{a}}^{x-c_k\tilde{a}} \mathcal{D}x_k(t) e^{-S_k[x_k(t),0]} \quad (5.46)$$

$$= \int_{-\infty}^{\infty} dx \int_x^x \mathcal{D}x_k(t) e^{-S_k[x_k(t),0]} \quad (5.47)$$

$$\equiv I_k, \quad \text{which is independent of } \tilde{a}. \quad (5.48)$$

Here, in Eq. (5.46), we defined  $x_k(t) \equiv q_k(t) - c_k\tilde{a}$  and we have used the relation  $S_k[q_k(t), \tilde{a}] = S_k[x_k(t), 0]$  (Eq. (5.44)).

Hence, just like in the case of the CL model, we again have that  $I[\tilde{a}] \equiv I$  is independent of  $\tilde{a}$ . This again leads to the familiar CL-USC result (Eq. (5.16)). This means that CL-USC result is valid for a larger class of open system model, namely for GCL2 model, as defined here.

### 5.3 Ultra-Strong Coupling Mean Force Gibbs State for Zwanzig model

We will now study the USC-MFGS for the so-called Zwanzig model [83–86], which has been previously studied in the context of Brownian motion and barrier crossing problems. Let the full SE Hamiltonian for the Zwanzig model be given as  $\hat{H}_{SE} = \hat{H}_S + \hat{H}_I$ , where  $\hat{H}_S$  is the free system Hamiltonian and  $\hat{H}_I$  is given as

$$\hat{H}_I = \sum_k^N \left[ \frac{\hat{p}_k^2}{2m_k} + U_k^{\text{free}}(\hat{q}_k) + \frac{c_k}{2} U_k(\hat{q}_k - \hat{A}) \right]. \quad (5.49)$$

Here  $U_k^{\text{free}}(q_k)$  is an arbitrary free potential of the  $k$ th environment particle and  $U_k(x)$  is as defined in Sec. 5.2.1, but with just one extra condition that  $U_k(x)$  now has a unique global minima point at  $x = x_k$  and if there is any other local minima at a point  $x = y_k$ , then we have, for some non-infinitesimal positive number  $\lambda$ ,

$$U_k(y_k) - U_k(x_k) \geq \lambda > 0. \quad (5.50)$$

In other words, we now assume that not only does  $U_k(x)$  have a unique global minimum, but also that if the potential has any other local minima, then there is a non-infinitesimal energy difference between the global minimum and the local minima. The significance of this assumption will become clear shortly.

Note that in Sec. 5.2.1, the interaction potential was of the form  $U_k(\hat{q}_k - c_k \hat{A})$  while here, it is of the form  $c_k U_k(\hat{q}_k - \hat{A})$ . Hence, the Zwanzig model is microscopically motivated to have a spring-like interaction between the system and the environment particles. In fact, if  $U_k(x)$  is a harmonic potential, then  $c_k$  can be interpreted as the stiffness constant of the corresponding spring. Also note that here, we have deliberately not added a counter term in the interaction Hamiltonian because any renormalization of the system's free Hamiltonian will be assumed here to be of physical origin.

Now, the path integral expression for the MFGS will be given exactly as in CL model (Eq. (2.156) and Eq. (2.157)), where the action associated with  $I_k[A(t)]$  will now be given as

$$S_k[q_k(t), A(t)] \equiv \int_0^\beta dt \left\{ \frac{m_k}{2} \dot{q}_k(t)^2 + U_k^{\text{free}}(q_k(t)) + \frac{c_k}{2} U_k(q_k(t) - A(t)) \right\}. \quad (5.51)$$

In the USC limit (Eq. (5.9)), for paths that contribute significantly to the path integral, the condition

$$q_k(t) = A(t) + x_k \quad (5.52)$$

will get strictly imposed here. This is because as discussed in the context of the GCL2 model,  $U_k(x_k) = 0$  is defined as the global minima of the potential  $U_k(x)$  (Eq. (5.42)) and we have further assumed that for Zwanzig model, this global minimum is unique and has a non-infinitesimal energy difference from any other local minima that might be there

(Eq. (5.50)). Hence, in the USC limit, we will have

$$\lim_{c_k \rightarrow \infty} \exp \{-c_k U_k(x)\} = \begin{cases} 0 & \text{for } x \neq x_k \\ 1 & \text{for } x = x_k \end{cases}. \quad (5.53)$$

Replacing Eq. (5.52) in Eq. (5.51), the corresponding influence functional (Eq. (2.157)) becomes

$$I_k[A(t)] = e^{-\int_0^\beta dt \left\{ \frac{m_k}{2} \dot{A}(t)^2 + U_k^{\text{free}}(A(t) + x_k) \right\}}. \quad (5.54)$$

Since the influence functional  $I_k[A(t)]$  (Eq. (2.157)) arises when we take partial trace over the environment degrees of freedom, the environment side paths,  $q_k(t)$ , come with a constraint that  $q_k(0) = q_k(\beta)$ . In the USC limit, since  $q_k(t)$  gets further constrained as  $q_k(t) = A(t) + x_k$  (Eq. (5.52)), this in turn puts a constraint that for paths that contribute to the path integral,  $A(0) = A(\beta)$ . This effectively diagonalizes the final USC-MFGS in the basis of the system coupling operator  $\hat{A}$ , but through a mathematical mechanism that is different from the one encountered in the GCL model.

### 5.3.1 Special Case 1: Discrete system

If the system lives in a discrete Hilbert space,  $A(t)$  generally has instantaneous jumps, in which case the kinetic term in the action in  $I_k[A(t)]$  will blow up (Eq. (5.54)), preventing the jump. Hence, for a discrete system, paths with an instantaneous jump will be suppressed and we will have  $\dot{A}(t) = 0$ .

Next, for  $A(t) = \tilde{a}$ , the influence functional (Eq. (5.54)) simplifies as

$$\implies I_k[\tilde{a}] = \exp \left\{ - \int_0^\beta dt U_k^{\text{free}}(\tilde{a} + x_k) \right\} \quad (5.55)$$

$$= \exp \left\{ -\beta U_k^{\text{free}}(\tilde{a} + x_k) \right\}. \quad (5.56)$$

Replacing this in the full MFGS path integral expression (Eq. (2.156)) gives

$$\rho_{\text{USC}}(a, b) = \tilde{Z}^{-1} e^{-\beta U_{\text{eff}}(\tilde{a})} \int_a^b \mathcal{D}\phi(t) \exp \{ -S_S[\tilde{a}, \phi(t)] \}. \quad (5.57)$$

Here  $a$  and  $b$  are the eigenvalues of the operator  $\hat{\phi}$  and  $\tilde{a}$  is the eigenvalue of  $\hat{A}$  [116] and  $U_{\text{eff}}(x)$  is defined as

$$U_{\text{eff}}(x) \equiv \sum_{k=1}^N U_k^{\text{free}}(x + x_k). \quad (5.58)$$

Finally, the USC-MFGS is given as,

$$\implies \hat{\rho}_{\text{USC}} = Z^{-1} \exp \{ -\beta \tilde{H} \} \quad (5.59)$$

$$\tilde{H} \equiv \sum_i \hat{P}_i (\hat{H}_S + \hat{V}_0) \hat{P}_i. \quad (5.60)$$

Here  $\hat{P}_i$  is the projection operator on the  $i$ th degenerate subspaces of the operator  $\hat{A}$  with eigenvalue  $A_i$ . Here  $\hat{V}_0$  is defined as

$$\hat{V}_0 = \sum_i U_{\text{eff}}(A_i) \hat{P}_i. \quad (5.61)$$

Hence, effectively, this is just the USC-MFGS result for the GCL model, but with a renormalized free system Hamiltonian (Eq. (5.60)).

### 5.3.2 Special Case 2: Continuous Variable system

Now, assume that we are dealing with a CV system, where we have a particle with mass  $m$  in a potential  $V(q)$ . Then, the free Hamiltonian  $\hat{H}_S$  is given as

$$\hat{H}_S = \frac{\hat{p}^2}{2m} + V(\hat{q}). \quad (5.62)$$

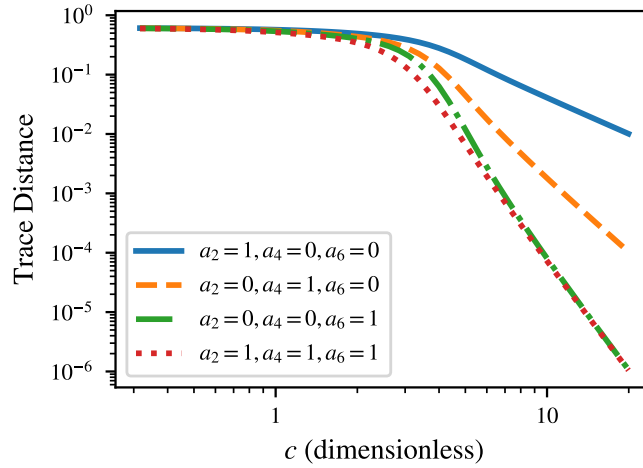


Figure 5.2: The trace distance between the USC-MFGS for the GCL2 model (see Eq. (5.16)) and the numerically evaluated MFGS (see Eq. (1.1)) as a function of the coupling strength  $c$  (see Eq. (5.69)), for different choices of the interaction potential (Eq. (5.70)). This shows that in the large- $c$  limit, the USC-MFGS for the restricted case of a system interacting with a single anharmonic environment approaches the same state despite the different interaction potentials used.

Also, for simplicity, assume that the system coupling-operator is given as  $\hat{A} = \hat{q}$ . Then, using the simplified expression for the influence functional for Zwanzig model (Eq. (5.54)) in the full MFGS path integral (Eq. (2.156)) gives the USC-MFGS as

$$\rho_{\text{USC}}(x, y) = \tilde{Z}^{-1} \delta(x, y) \int_x^y \mathcal{D}q(t) \exp \left\{ - \int_0^\beta dt \left( \frac{1}{2} M_{\text{eff}} \dot{q}(t)^2 + V_{\text{eff}}(q(t)) \right) \right\} \quad (5.63)$$

where,

$$M_{\text{eff}} = m + \sum_k m_k \quad (5.64)$$

$$V_{\text{eff}}(x) = V(x) + U_{\text{eff}}(x) \quad (5.65)$$

The USC-MFGS can now be determined as

$$\langle q | \hat{\rho}_{\text{USC}} | q' \rangle = Z^{-1} \delta(q, q') \langle q | e^{-\beta \hat{H}_{\text{eff}}} | q' \rangle, \quad (5.66)$$

$$\hat{H}_{\text{eff}} = \frac{\hat{p}^2}{2M_{\text{eff}}} + V_{\text{eff}}(\hat{q}). \quad (5.67)$$

Note one key distinction here from the GCL2-USC result, in that although both the states are diagonal in the basis set by the system coupling-operator, the corresponding GCL2-USC result for CV system would be of the form,  $\hat{\rho}_{\text{USC-GCL2}} = Z^{-1}e^{-\beta V_{\text{eff}}(\hat{q})}$ , as derived in Sec. 5.5.3. [22, 81, 108] The Zwanzig-USC result (Eq. (5.66)) will converge to the GCL2 result only when  $M_{\text{eff}} \rightarrow \infty$ , which will suppress paths of the type  $\dot{q}(t) \neq 0$  in the path integral. This will typically not be the case for a system interacting with a few environment particles or particles that are not very massive, for example.

We note that there has been a disagreement in the literature regarding the form of the USC equilibrium state under the CL model. [22] For the CL model, Kawai et al. conjectured [119, 120] the system's dynamical state at long times to be  $\hat{\rho}^{\text{conj}} = \sum_i \hat{P}_i e^{-\beta \hat{H}_0} \hat{P}_i$  and we note that, coincidentally, the Zwanzig-USC result for CV systems (Eq. (5.66)) is similar to this conjectured form.

## 5.4 Numerical verification

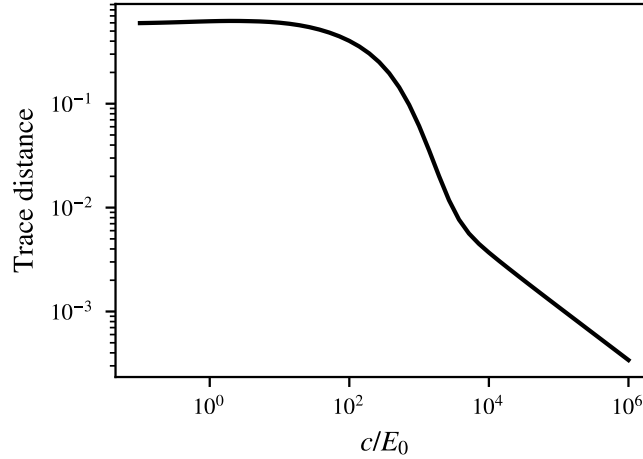


Figure 5.3: The trace distance between the USC-MFGS for the Zwanzig model (see Eq. (5.59)) and the numerically calculated MFGS (see Eq. (1.1)) as a function of the coupling strength  $c$  (see Eq. (5.71)). This verifies that the numerically evaluated USC-MFGS for the Zwanzig model (for the restricted case of a quantum system interacting with a single environmental particle) approaches our analytical result in the large- $c$  limit.

In this section, we conduct numerical tests to validate the analytical results presented in

this paper. Specifically, we verify the USC-MFGS results for both the GCL2 (Eq. (5.16)) and the Zwanzig model (Eq. (5.59)). Additionally, we examine how the convergence rate of the MFGS towards the USC results varies with an increase in the SE coupling, across different model parameters.

For both the GCL2 and Zwanzig models, we numerically consider a simplified scenario involving a qutrit system interacting with a single environmental particle. We note that a quantum system interacting with just one bosonic mode is a very unphysical model of an open quantum system. Yet, this serves as a useful numerical verification of the analytical results presented here for two reasons. First, as we have seen, in all of the results considered in this chapter, the environmental modes individually cause the system paths in the imaginary time path integral to freeze. Hence, studying the imaginary-time path integral in the presence of just one environmental mode serves as a verification of the central idea presented in this chapter. Second, having just one environmental mode allows for the convenient numerical evaluation of the exact MFGS, denoted by  $\hat{\rho}_{\text{num}}$  (see Sec. 5.5.2 for numerical details).

The system free Hamiltonian,  $\hat{H}_S$ , and the system coupling-operator,  $\hat{A}$ , are fixed throughout to be

$$\hat{H}_S = \begin{pmatrix} 1 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & -1 \end{pmatrix}, \quad \hat{A} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -0.5 \end{pmatrix}. \quad (5.68)$$

We set  $\beta = 5$  throughout. For the GCL model, the interaction Hamiltonian,  $\hat{H}_I$ , (Eq. (5.18)) simplifies as

$$\hat{H}_I = \frac{\hat{P}^2}{2M} + V\left(\frac{\hat{Q}}{L_0} - c\hat{A}\right). \quad (5.69)$$

Here,  $M = 1$  and  $L_0 = 1$  is a unit of length. Hence,  $c$  is a dimensionless quantity.  $V(x)$  is

assumed to be of the form

$$V(x) = \sum_{n=1}^3 a_{2n} x^{2n}. \quad (5.70)$$

Fig. 5.2 plots the trace distance between  $\hat{\rho}_{\text{num}}$  and  $\hat{\rho}_{\text{USC}}$  (Eq. (5.16)) for this model as we increase the coupling parameter,  $c$ , for different values of the positive semi-definite coefficients  $a_{2n}$ . We generically find that, as expected, the trace distance drops quickly as the value of  $c$  is increased. We also find that higher order SE coupling causes the MFGS to approach the USC state faster as a function of the coupling parameter  $c$ .

This behavior can be explained for a generic GCL model if we note that a path  $A(t)$  will contribute significantly to the path integral only if we have  $\sigma_A = O(\Delta/c_k)$ . For the USC limit, we therefore require that  $\Delta/c_k \ll 1$ . Hence, the USC limit is approached based on the interplay between the coupling parameter  $c_k$  and  $\Delta$ . [121] So, if  $\Delta$  is small for some coupling potential  $V_k(x, y)$ , like in the case of the potentials with  $a_4 = 1$  or  $a_6 = 1$  in Fig. 5.2, then it will facilitate the approach to the USC limit.

Next, for Zwanzig model, the interaction Hamiltonian  $\hat{H}_I$  (Eq. (5.49)) is assumed to be

$$\hat{H}_I = \frac{\hat{P}^2}{2M} + U(\hat{Q}) + \frac{c}{2} \left( \frac{\hat{Q}}{L_0} - \hat{A} \right)^2. \quad (5.71)$$

Here,  $M = 1$ ,  $L_0 = 1$  is a unit of length. Hence,  $c$  is the unit of energy.  $U(x)$  is a Morse potential given by

$$U(x) \equiv (1 - e^{-x/L_0})^2. \quad (5.72)$$

Fig. 5.3 plots the trace distance between  $\hat{\rho}_{\text{num}}$  and  $\hat{\rho}_{\text{USC}}$  (Eq. (5.59)) for this model as we increase the value of the coupling parameter,  $c$ . We again observe that, as expected, the trace distance drops quickly as the value of  $c$  is increased, though the rate of approach to the USC result is much slower than the GCL case.

## 5.5 Technical Details

**Proposition 5.** *Let  $f(t)$  be a continuous, differentiable and square integrable function such that its derivative,  $\dot{f}(t)$ , is also square integrable, such that*

$$f(t) \equiv g(t) + \epsilon(t). \quad (5.73)$$

*Here  $g(t)$  is also square integrable. Next, for some  $\Delta > 0$ , we have the constraint that*

$$|\epsilon(t)| < \Delta. \quad (5.74)$$

*Next, let us define*

$$\langle g \rangle \equiv \frac{1}{\beta} \int_0^\beta dt g(t), \quad (5.75)$$

$$\langle g^2 \rangle \equiv \frac{1}{\beta} \int_0^\beta dt g(t)^2, \quad (5.76)$$

$$\sigma_g^2 \equiv \langle g^2 \rangle - \langle g \rangle^2. \quad (5.77)$$

*Then, in the limit  $\sigma_g^2 \gg \Delta^2$ , we will prove that*

$$\frac{1}{\beta} \int_0^\beta dt \dot{f}(t)^2 \geq \mu \frac{\sigma_g^2}{\beta^2}, \quad (5.78)$$

*where  $\mu > 0$  is a constant.*

*Proof.* The intuitive idea behind the proof is this. Part 1 of the proof consists of proving that

$$\lim_{\sigma_g^2 \gg \Delta^2} \sigma_f^2 \approx \sigma_g^2. \quad (5.79)$$

Part 2 then consists of proving that given  $\sigma_f$ ,

$$\frac{1}{\beta} \int_0^\beta dt \dot{f}(t)^2 \geq \mu \sigma_f^2 / \beta^2, \quad \text{where } \mu > 0. \quad (5.80)$$

Replacing Eq. (5.79) into Eq. (5.80) then gives the final result (Eq. (5.78)).

Both these claims are intuitive, as the first claim states that if the absolute difference between two functions is much smaller than the standard deviation of one of the functions, then their standard deviations are also approximately equal. The second claim states that, for a function  $f(t)$ , if  $\sigma_f^2 > 0$ , then  $\langle \dot{f}^2 \rangle > 0$  and also that  $\langle \dot{f}^2 \rangle \propto \sigma_f^2$ , which makes sense because if you scale a function as  $f(t) \rightarrow 2f(t)$ , then we have  $\sigma_f^2 \rightarrow 4\sigma_f^2$  and  $\langle \dot{f}^2 \rangle \rightarrow 4\langle \dot{f}^2 \rangle$ .

**Part 1 of the proof:** Let us calculate  $\sigma_f^2$  (using Eq. (5.73)) as

$$\sigma_f^2 = \langle (g + \epsilon)^2 \rangle - \langle g + \epsilon \rangle^2 \quad (5.81)$$

$$= \langle g^2 \rangle + 2\langle g\epsilon \rangle + \langle \epsilon^2 \rangle - (\langle g \rangle^2 + 2\langle g \rangle \langle \epsilon \rangle + \langle \epsilon \rangle^2) \quad (5.82)$$

$$= \sigma_g^2 + \sigma_\epsilon^2 + 2(\langle g\epsilon \rangle - \langle g \rangle \langle \epsilon \rangle) \quad (5.83)$$

$$\leq \sigma_g^2 + O(\Delta^2) + 2\sigma_g O(\Delta). \quad (5.84)$$

Here, we used  $\langle g\epsilon \rangle - \langle g \rangle \langle \epsilon \rangle \leq \sigma_g \sigma_\epsilon$  that can be derived using the Cauchy-Schwarz inequality. Finally, in the limit  $\sigma_g^2 \gg \Delta^2$ , we get the required result (Eq. (5.79)).

**Part 2 of the proof:** Proof of Eq. (5.80) follows directly from Poincaré inequality [122, 123] that can be formally stated as following. [124]

**Lemma 1** (Poincaré inequality). *Let  $\Omega$  be an open, bounded, and connected subset of  $\mathbb{R}^d$  for some  $d$  and let  $d\mathbf{x}$  denote  $d$ -dimensional Lebesgue measure on  $\mathbb{R}^d$ . Then the Poincaré inequality says that there exist constants  $C_1$  and  $C_2$  such that*

$$\int_\Omega h^2(\mathbf{x}) d\mathbf{x} \leq C_1 \int_\Omega |\nabla h(\mathbf{x})|^2 d\mathbf{x} + C_2 \left[ \int_\Omega h(\mathbf{x}) d\mathbf{x} \right]^2, \quad (5.85)$$

for all functions  $h$  in the Sobolev Space  $H^1(\Omega)$  consisting of all functions in  $L^2(\Omega)$  whose generalized derivatives are all also square integrable.

For 1-dimensional Euclidean space, for simplicity and without loss of any generality, let us redefine  $f(t)$  such that  $\langle f \rangle = 0$ . In other words, we shift  $f(t) \rightarrow f(t) - \langle f \rangle$ . Then, the Poincaré inequality implies that

$$\langle f^2 \rangle \leq C_1 \langle \dot{f}^2 \rangle + \beta C_2 \langle f \rangle^2 \quad (5.86)$$

$$\implies \sigma_f^2 \leq C_1 \langle \dot{f}^2 \rangle. \quad (5.87)$$

Since  $\sigma_f^2 \geq 0$  and  $\langle \dot{f}^2 \rangle \geq 0$ , we have that  $C_1$  is positive. We therefore have

$$\langle \dot{f}^2 \rangle \geq \frac{\beta^2}{C_1} \frac{\sigma_g^2}{\beta^2}. \quad (5.88)$$

This proves Eq. (5.80) for  $\mu = \beta^2/C_1$  and concludes the proof of the main result (Eq. (5.78)).

□

### 5.5.1 Proof of special case of Poincaré Inequality

Here, for completeness, we provide a proof for the special case of Poincaré inequality (Eq. (5.80)), as per the present requirement. To simplify the proof, other than assuming that  $\langle f \rangle = 0$ , we also shift the range of the imaginary time from the conventional  $0 \leq t \leq \beta$  to  $-\beta/2 \leq t \leq \beta/2$ . Now, given a constraint

$$\int_{-\beta/2}^{\beta/2} f(t)^2 dt = \beta \sigma_f^2, \quad (5.89)$$

we need to minimize over the action

$$S = \int_{-\beta/2}^{\beta/2} dt \dot{f}(t)^2 \quad (5.90)$$

subject to the constraint that  $\langle f \rangle = 0$ , which implies

$$\int_{-\frac{\beta}{2}}^{\frac{\beta}{2}} dt f(t) = 0, \quad (5.91)$$

and subject also to the boundary conditions

$$f\left(-\frac{\beta}{2}\right) = 0 = f\left(\frac{\beta}{2}\right). \quad (5.92)$$

We do this by perturbing the optimum path by a small amount,  $f(t) \rightarrow f(t) + \delta(t)$ , with  $\delta(-\beta/2) = \delta(\beta/2) = 0$ . Then Eq. (5.89) demands that to the first order in  $\delta(t)$ , we have

$$\int_{-\frac{\beta}{2}}^{\frac{\beta}{2}} f(t) \delta(t) dt = 0. \quad (5.93)$$

Now, the condition for the minimum action is  $\delta S = 0$ , where

$$\frac{\delta S}{2} = \int_{-\frac{\beta}{2}}^{\frac{\beta}{2}} dt \dot{f}(t) \dot{\delta}(t) \quad (5.94)$$

$$= \dot{f}(\beta/2) \delta(\beta/2) - \dot{f}(-\beta/2) \delta(-\beta/2) - \int_{-\frac{\beta}{2}}^{\frac{\beta}{2}} dt \ddot{f}(t) \delta(t) \quad (5.95)$$

$$= - \int_{-\frac{\beta}{2}}^{\frac{\beta}{2}} dt \ddot{f}(t) \delta(t) = 0. \quad (5.96)$$

Comparing Eq. (5.96) with Eq. (5.93), for some constant  $\lambda$ , we get

$$\ddot{f}(t) = \pm \lambda^2 f(t). \quad (5.97)$$

The solution of  $f(t)$  can be either sinusoidal or hyperbolic type. For the sinusoidal solution, we have

$$f(t) = A \sin(\lambda t + \phi). \quad (5.98)$$

Then the condition,  $\langle f \rangle = 0$ , demands that

$$\int_{-\frac{\beta}{2}}^{\frac{\beta}{2}} A \sin(\lambda t + \phi) dt = 0 \quad (5.99)$$

$$\implies -\frac{A}{\lambda} \left( \cos\left(\frac{\lambda\beta}{2} + \phi\right) - \cos\left(-\frac{\lambda\beta}{2} + \phi\right) \right) = 0 \quad (5.100)$$

$$\implies \cos\left(\frac{\lambda\beta}{2} + \phi\right) = \cos\left(-\frac{\lambda\beta}{2} + \phi\right). \quad (5.101)$$

The solution is either, for a generic  $\lambda$ ,  $\phi = 0$  or for a generic  $\phi$ ,  $\lambda = 2\pi n/\beta$  for  $n \in \mathbb{Z}$ . Hence, we have

$$f(t) = \begin{cases} A \sin(\lambda t) & \text{for generic } \lambda \\ A \sin(\lambda t + \phi) & \text{for } \lambda = 2\pi n/\beta; \quad n \in \mathbb{Z} \end{cases}. \quad (5.102)$$

For hyperbolic solution,  $f(t)$  is given as

$$f(t) = A \sinh(\lambda t). \quad (5.103)$$

Here, we do not have a cosh kind of term. This follows from the requirement that  $\langle f \rangle = \int_{-\beta/2}^{\beta/2} dt f(t) = 0$ .

### Sinusoidal solution

Let us first consider the solution for  $\phi = 0$  and a generic  $\lambda$

$$f(t) = A \sin(\lambda t) \quad (5.104)$$

$$\implies \beta \langle f^2 \rangle = A^2 \int_{-\frac{\beta}{2}}^{\frac{\beta}{2}} \sin^2(\lambda t) dt \quad (5.105)$$

$$= \frac{A^2}{2} \int_{-\frac{\beta}{2}}^{\frac{\beta}{2}} 1 - \cos(2\lambda t) dt \quad (5.106)$$

$$= \frac{A^2}{2} \left( \beta - \frac{2 \sin(\lambda\beta)}{2\lambda} \right) \quad (5.107)$$

$$= \frac{A^2\beta}{2} \left( 1 - \frac{\sin(x)}{x} \right) \quad ; x \equiv \lambda\beta \quad (5.108)$$

$$\implies A^2 = \langle f^2 \rangle \frac{2x}{x - \sin(x)}. \quad (5.109)$$

This expression for  $A^2$  is crucial, so let us also evaluate it for the case when, in Eq. (5.104),  $\phi$  is present and  $\lambda = 2\pi n/\beta$  for  $n \in \mathbb{Z}$ .

$$f(t) = A \sin\left(\frac{2\pi nt}{\beta} + \phi\right) \quad (5.110)$$

$$\implies \beta \langle f^2 \rangle = A^2 \int_{-\frac{\beta}{2}}^{\frac{\beta}{2}} \sin^2\left(\frac{2\pi nt}{\beta} + \phi\right) dt \quad (5.111)$$

$$= \frac{A^2\beta}{2} \quad (5.112)$$

$$\implies A^2 = 2 \langle f^2 \rangle \quad (5.113)$$

$$= \langle f^2 \rangle \frac{2x}{x - \sin(x)} \Big|_{x=2\pi n} \quad (5.114)$$

This is consistent with Eq. (5.109). Hence, Eq. (5.109) holds generically for the full sinusoidal case. Next, we have that

$$f(t)^2 + \frac{\dot{f}(t)^2}{\lambda^2} = A^2 \quad (5.115)$$

$$\implies \langle f^2 \rangle + \frac{\langle \dot{f}^2 \rangle}{\lambda^2} = A^2 \quad (5.116)$$

$$\implies \langle \dot{f}^2 \rangle = \lambda^2 (A^2 - \langle f^2 \rangle) \quad (5.117)$$

$$= \frac{x^2}{\beta^2} \left( \langle f^2 \rangle \frac{2x}{x - \sin(x)} - \langle f^2 \rangle \right) \quad (5.118)$$

$$= \frac{\langle f^2 \rangle}{\beta^2} x^2 \left( \frac{x + \sin(x)}{x - \sin(x)} \right) \quad (5.119)$$

$$\geq \left( \min_x h_{\sin}(x) \right) \frac{\langle f^2 \rangle}{\beta^2}. \quad (5.120)$$

Here

$$h_{\sin}(x) \equiv x^2 \left( \frac{x + \sin(x)}{x - \sin(x)} \right). \quad (5.121)$$

Note that  $\min_x h_{\sin}(x) > 0$ , which can also be seen from Fig. 5.4. Eq. (5.120) is the desired result for the sinusoidal case.

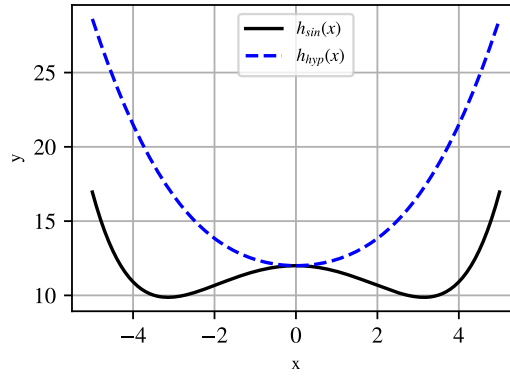


Figure 5.4: Plot of  $h_{\sin}(x)$  (Eq. (5.121)) and  $h_{\text{hyp}}(x)$  (Eq. (5.131)), which demonstrates that the minima of both these functions are larger than zero. The minima of the functions  $h_{\sin}(x)$  and  $h_{\text{hyp}}(x)$  represent the coefficients of the restricted case of the Poincare inequality (Eq. (5.87)), which needs to be greater than zero for Proposition 5 to hold. The current figure demonstrates this.

## Hyperbolic solution

Let

$$f(t) \equiv A \sinh(\lambda t) \quad (5.122)$$

$$\beta \langle f^2 \rangle \equiv A^2 \int_{-\frac{\beta}{2}}^{\frac{\beta}{2}} \sinh^2(\lambda t) dt \quad (5.123)$$

$$= -\frac{A^2}{2} \int_{-\frac{\beta}{2}}^{\frac{\beta}{2}} 1 - \cosh(2\lambda t) dt \quad (5.124)$$

$$\implies A^2 = -\langle f^2 \rangle \frac{2x}{x - \sinh(x)}. \quad (5.125)$$

Here, in the last step, we used the analogous derivation from Eq. (5.106) to Eq. (5.109), but with an extra minus sign. Now, note that we have

$$\frac{\dot{f}(t)^2}{\lambda^2} - f(t)^2 = A^2 \quad (5.126)$$

$$\implies \frac{\langle \dot{f}^2 \rangle}{\lambda^2} - \langle f^2 \rangle = A^2 \quad (5.127)$$

$$\implies \langle \dot{f}^2 \rangle = -\lambda^2 (-A^2 - \langle f^2 \rangle) \quad (5.128)$$

$$= -\frac{x^2}{\beta^2} \left( \langle f^2 \rangle \frac{2x}{x - \sinh(x)} - \langle f^2 \rangle \right) \quad (5.129)$$

$$\geq \left( \min_x h_{\text{hyp}}(x) \right) \frac{\langle f^2 \rangle}{\beta^2}. \quad (5.130)$$

In the last step, we used the analogous calculation from Eq. (5.118) to Eq. (5.120), with just an extra minus sign. Here,  $h_{\text{hyp}}(x)$  is defined as

$$h_{\text{hyp}}(x) \equiv x^2 \left( \frac{\sinh(x) + x}{\sinh(x) - x} \right). \quad (5.131)$$

Note that  $\min_x h_{\text{hyp}}(x) > 0$ , which can also be seen from Fig. 5.4. Eq. (5.130) is the desired result for the hyperbolic case.

**Proposition 6.** *Let  $f(x)$  be a continuous and differentiable function and let us define  $h(x) \equiv \frac{d}{dx} f(x)$  such that*

$$h(x) \geq \Omega_0, \quad (5.132)$$

*for some positive constant  $\Omega_0$ . Now, let  $g(t)$  be a square integrable function and let the following quantities be well defined:*

$$\langle f \circ g \rangle \equiv \frac{1}{\beta} \int_0^\beta dt f(g(t)) \quad (5.133)$$

$$\langle (f \circ g)^2 \rangle \equiv \frac{1}{\beta} \int_0^\beta dt f(g(t))^2 \quad (5.134)$$

$$\sigma_{f \circ g}^2 \equiv \langle (f \circ g)^2 \rangle - \langle f \circ g \rangle^2. \quad (5.135)$$

Then, we will prove that

$$\sigma_{f \circ g}^2 \geq \Omega_0^2 \sigma_g^2, \quad (5.136)$$

where  $\sigma_g^2$  is defined analogously (Eq. (5.77)).

*Proof.* Using the Mean-Value Theorem, for some  $x'$  such that  $x_0 < x' < x_1$ , we have

$$f(x_1) - f(x_0) = h(x')(x_1 - x_0) > 0 \quad (5.137)$$

$$\geq \Omega_0(x_1 - x_0) > 0 \quad (5.138)$$

$$\implies f(x_0) - f(x_1) \leq \Omega_0(x_0 - x_1) < 0 \quad (5.139)$$

$$\implies |f(b) - f(a)| \geq \Omega_0|b - a| \quad \forall a, b. \quad (5.140)$$

$$\implies |(f \circ g)(t) - (f \circ g)(s)| \geq \Omega_0|g(t) - g(s)| \quad \forall t, s. \quad (5.141)$$

Now, we introduce the symmetric definition of variance for a function  $X(t)$  as

$$\sigma_X^2 = \frac{1}{2\beta^2} \int_0^\beta \int_0^\beta (X(t) - X(s))^2 dt ds. \quad (5.142)$$

We use this to write:

$$\sigma_{f \circ g}^2 = \frac{1}{2\beta^2} \int_0^\beta \int_0^\beta ((f \circ g)(t) - (f \circ g)(s))^2 dt ds, \quad (5.143)$$

$$\geq \frac{\Omega_0^2}{2\beta^2} \int_0^\beta \int_0^\beta (g(t) - g(s))^2 dt ds \quad (5.144)$$

$$= \Omega_0^2 \sigma_g^2. \quad (5.145)$$

□

### 5.5.2 Numerical details

The Hamiltonian of a qutrit system coupled to a single anharmonic oscillator (Eq. (5.68) together with Eq. (5.69) (for GCL2 model) and Eq. (5.71) (for Zwanzig-model)) is essentially an infinite-dimensional operator. In order to numerically evaluate the MFGS,

$$\hat{\rho} = Z^{-1} \text{Tr}_E \left[ e^{-\beta \hat{H}_{SE}} \right], \quad (5.146)$$

We truncate the position operator  $\hat{Q}$  of the environment oscillator so that its eigenvalues  $Q$  is restricted to  $Q_{min} \leq Q \leq Q_{max}$ . We also discretize  $\hat{Q}$  into  $N$  discrete points. This effectively approximates the original infinite-dimensional Hamiltonian  $\hat{H}_{SE}$  to one with  $3N$  dimensions.

It is now possible to numerically evaluate the MFGS (Eq. (5.146)). We vary the values of  $Q_{min}$ ,  $Q_{max}$  and  $N$  until the final result of interest converges (in this case, the trace distance between  $\hat{\rho}_{num}$  and  $\hat{\rho}_{USC}$ ).

### 5.5.3 Ultra-Strong Coupling Mean Force Gibbs State for Continuous Variable System

In the case of a CV system, if we consider the free Hamiltonian  $\hat{H}_S$  to be given by

$$\hat{H}_S = \frac{\hat{p}^2}{2m} + V(\hat{q}), \quad (5.147)$$

with  $\hat{A} \equiv \hat{q}$ , then the projectors  $\hat{P}_i$  in Eq. (5.17) will be replaced by  $|q\rangle \langle q|$  and the summation over  $i$  will be replaced by an integral over the eigenvalue  $q$ , giving rise to

$$\tilde{H} = \int dq \langle q | \hat{H}_S | q \rangle |q\rangle \langle q| \quad (5.148)$$

$$= \int \frac{1}{2m} \langle q | \hat{p}^2 | q \rangle |q\rangle \langle q| dq + \int V(q) |q\rangle \langle q| dq. \quad (5.149)$$

Since both the terms in Eq. (5.149) commute with each other, the corresponding USC-MFGS (Eq. (5.16)) is given as

$$\hat{\rho}_{\text{USC}} = Z^{-1} \exp \{ -\beta \tilde{H} \} \quad (5.150)$$

$$= Z^{-1} e^{-\beta V(\hat{q})} \exp \left\{ -\frac{\beta}{2m} \int \langle q | \hat{p}^2 | q \rangle |q\rangle \langle q| dq \right\}. \quad (5.151)$$

Now, we have  $\langle q | \hat{p}^2 | q \rangle = \langle q + a | \hat{p}^2 | q + a \rangle$  for all real  $a$ . Therefore, the operator

$$\exp \left\{ -\frac{\beta}{2m} \int \langle q | \hat{p}^2 | q \rangle |q\rangle \langle q| dq \right\}$$

is proportional to the identity operator and can be absorbed into the trace. We therefore get the USC-MFGS for CV system as [81]

$$\hat{\rho}_{\text{USC}} = Z'^{-1} e^{-\beta V(\hat{q})}. \quad (5.152)$$

# Chapter 6

## Conclusions

The results of this thesis can be broadly categorised into two main themes:

- Derivation, study and application of the complete analytical form of the fourth-order time-convolutionless generator for the generic spin-boson model valid for a large class of environmental spectral densities (see Chapters [3](#) and [4](#)).
- Extension of the ultra-strong coupling mean force Gibbs state from Harmonic to a large class of anharmonic environment (see Chapter [5](#)).

These results hence encompass a wide range of physical systems and phenomena, going beyond the typical weak coupling assumption for the open quantum systems. Now, we discuss the implications of these results and future directions in detail in the following sections.

## 6.1 Time-Convolutionless Fourth-Order Generator for the Spin-Boson Model (Chapters 3 and 4)

In this work, we have derived the complete analytical form of the asymptotic TCL4 generator,  $F^{(4)}$ , for the generic spin-boson model, for a very broad class of environmental spectral densities,  $J(\omega)$ . The key results of this work are:

- We have derived the expressions for the TCL4 generator in terms of a single or double integral over frequencies (see Eq. (3.34) and Sec. 4.4.2), which cannot be further simplified without knowing the explicit form of the spectral density.
- This has enabled us to evaluate the expressions for the 2nd and 4th order correction to the steady state population and coherences, respectively, for the generic SBM (see Sec. 4.4.2). We also show that the 2nd order correction to the steady-state population is equivalent to the corresponding mean force Gibbs state quantity.
- The full  $F^{(4)}$  generator enables the calculation of the complete temporal dynamics of the SBM up to  $O(\lambda^4)$  in the system-environment coupling strength  $\lambda$ . For example, application to a double quantum dot system demonstrates that TCL4 dynamics provides corrections to the dynamics that may be of experimental relevance under some parameter regimes (see Sec. 4.1).
- We report that for Ohmic spectral density with Drude cutoff, over a large range of temperature  $T$  and cutoff frequency  $\Lambda$ , TCL2 overestimates the non-Markovianity of the dynamics (see Fig. 4.2).
- The analytical expressions for the  $F^{(4)}$  generator were rigorously validated through consistency checks against specialised calculations for the Ohmic spectral density with Drude cutoff and by benchmarking the predicted dynamics against the numerically exact hierarchical equation of motion technique.

All the results mentioned in this work, including symbolic derivations, final expressions, numerical evaluation for specific parameters, and plots, etc., are publicly available in their complete form as the accompanying Supplementary material [52].

These results can serve as a valuable tool for theoretical investigations of a wide array of physical systems and phenomena modelled by the generic SBM [6, 7, 34–38]. It provides a means to explore dynamics in regimes where TCL2 is insufficient, without resorting to computationally intensive methods like HEOM and tensor network approaches (see, for example, [13] regarding this ‘computational intensiveness’).

Future research directions could include efforts to expand the class of spectral density for which our results are valid. Exploring the extension to even higher orders (e.g., TCL6 and beyond (see [12])) could be considered, though the analytical challenges are formidable. Furthermore, at finite temperature, the correspondence between the  $O(\lambda^4)$  corrections to SS coherences (derived in this work) and the corresponding MFGS quantity can also be checked, potentially shedding light on the conditions for their equivalence or divergence (the latter being indicated in [11] at zero temperature), a topic of ongoing interest.

## 6.2 Ultra-Strong Coupling Mean Force Gibbs State (Chapter 5)

The MFGS, defined in Eq. (1.1), has been studied in USC limit for a system coupled to an anharmonic environment, hence going beyond the corresponding known result for a harmonic environment, i.e. the CL model. For all the generalized SE models studied in this thesis, the USC-MFGS has been found to always be diagonal in the basis set by the SE interaction, although the exact form of the state differs from the CL-USC result, like in the case of the GCL model (Sec. 5.2). We also identify a subclass of the GCL model, which we call the GCL2 model (Sec. 5.2.1), for which the USC-MFGS remains equivalent

to the CL-USC result. This indicates robustness of the CL-USC result to certain types of anharmonic generalizations of the environment, but also highlights the sensitivity of the CL-USC result to other types of anharmonic generalizations. Furthermore, for a so-called Zwanzig model (distinct from the GCL model) (Sec. 5.3), analytical expression for the USC state has been derived and is found to have qualitative differences from the GCL-USC result (Eq. (5.66)).

These results demonstrate how the CL-USC result is influenced when the different assumptions of the model for which it was derived are relaxed one by one. In particular, these results directly extend the applicability of the CL-USC result for several strong coupling quantum thermodynamics, chemistry and biological problems where the anharmonicity of the environment becomes relevant. Also, our results indicate that anharmonicity of the environment has important implications on the rate of approach of the MFGS to the USC limit as a function of the coupling strength (Fig. 5.2). As a future direction, it would be interesting to apply our results to study some systems of physical interest (see for example [70, 77]).

The CL model has served as an important tool to model a variety of physical processes [2, 4, 34, 53–66], and its strengths and limitations in capturing the properties of these systems of interest have also been investigated. [78–80] Future research into extending such studies beyond the CL model (for example, to GCL2 and the Zwanzig model) will be of high interest. Moreover, the lines of reasoning used in this paper to obtain the USC-MFGS result can be applied to study USC-MFGS for other physically motivated generalized SE models.

Our results across a broad range of models indicate that the USC-MFGS invariably becomes diagonal in the basis of the system coupling-operator. Looking forward, it would be interesting to investigate whether this diagonalization is a universal feature of the USC-limit, independent of the further details of the SE model. Additionally, the CL-USC result has previously been expanded to first order in inverse of the SE coupling [125] and has

also been approximated for intermediate and weak coupling regime. [126, 127] Extending these results beyond the CL model would be a valuable direction for future research. Finally, for harmonic environments, the USC-MFGS has been shown to coincide with the steady state of the master equation [128]. Whether this equivalence holds for anharmonic environments remains an interesting future direction.

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