Reaction coordinate approach to non-Markovian dynamics in the spin-boson model

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The fundamental building blocks of quantum computers, called qubits, can be physically realized through any quantum system that is restricted to two possible states. The power of qubits arises from their ability to be in a superposition of these two states, allowing for the development of quantum algorithms that are impossible for classical computers. However, interactions with the surrounding environment destroy the superposition in a process called decoherence, which makes it important to find ways to model these interactions and mitigate them.

In this thesis we derive a non-Markovian master equation for the spin-boson model, with a time-dependent two-level system, using the reaction coordinate representation. We show numerically that in the superconducting qubit regime this master equation maintains the positivity of the density operator for relevant parameter ranges, and is able to model non-Markovian effects between the system and the environment. We also compare the reaction coordinate master equation to a Markovian master equation with parameters taken from real superconducting qubits. We demonstrate that the Markovian master equation fails to capture the system–bath correlations for short times, and in many cases overestimates relaxation and coherence times.

Finally, we test how a time-dependent bias affects the evolution of the two-level system. The bias is assumed to be constant with an additive term arising from an externally applied time-dependent plane wave control field. We show that an amplitude, angular frequency, and phase shift for the plane wave can be chosen such that the control field improves the coherence time of the two-level system.
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# Contents

Acknowledgements iii

Contents v

Notation vii

1 Introduction 1

2 Theoretical background 3
   2.1 Density operator formalism 3
   2.2 Open quantum systems 6
   2.3 Relaxation and dephasing rates 9
   2.4 Markovian and non-Markovian dynamics 10
   2.5 Spin-boson model 11
   2.6 Reaction coordinate 13

3 Reaction coordinate master equation 17
   3.1 Time-independent Hamiltonian 17
   3.2 Time-dependent two-level system 18
      3.2.1 Master equation for time-dependent control 19

4 Numerical results in the superconducting qubit regime 33
   4.1 Positivity of solutions 33
   4.2 Markovian master equation in the spin-boson model 35
   4.3 Comparison to Markovian dynamics 37
   4.4 Decay rates under decoherence 43

5 Discussion 47

Bibliography 49

A Computation of spin-boson spectral density 53
B  Eigenstates of a general two-level system 57
C  $\hat{B}_1(t)$ expectation value 61
D  Integration by parts of dissipation term 63
Notation

\( H \) Hilbert space of states
\( B(\mathcal{H}) \) space of bounded linear operators on \( H \)
\( T_1, T_2, T_\phi \) spin-lattice (longitudinal) relaxation time, spin-spin (transverse) relaxation time, and dephasing time which is given by \( \frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_\phi} \)
TLS two-level system
RC reaction coordinate system
B bosonic bath system, consisting of quantum harmonic oscillators
\( \varepsilon \) bias parameter of two-level system
\( \Delta \) tunnelling parameter of two-level system
\( \lambda \) interaction strength between the two-level system and the reaction coordinate
\( \Omega \) angular frequency of the reaction coordinate
\( \gamma \) interaction strength between the reaction coordinate and the residual bath
\( \alpha \) dimensionless coupling strength between the two-level system and the bath in the reaction coordinate framework, given by \( \alpha = 2\gamma\lambda^2/\Omega^2 \)
\( \hat{c}^\dagger_k, \hat{c}_k, \nu_k, f_k \) bosonic creation and annihilation operators for the \( k \)-th boson, its frequency in the bosonic bath, and its coupling strength with the two-level system
\( \hat{b}^\dagger_k, \hat{b}_k, \omega_k, g_k \) bosonic creation and annihilation operators for the \( k \)-th boson, its frequency in the residual bath, and its coupling strength with the reaction coordinate
\( \hat{a}^\dagger, \hat{a}, \hat{A} \) raising, lowering, and position operators of the reaction coordinate
\( \hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z \) the Pauli spin operators
\( J_{SB}(\nu), J_{RC}(\omega) \) spectral density functions describing the coupling between the spin and the bosonic bath, and the reaction coordinate and the residual bath
operators describing the coupling between the reaction coordinate and the residual bath

density operator, density operator of two-level system in the reaction coordinate model, density operator of two-level system in the Markovian model

the identity operator on the Hilbert space of system X

excited and ground state of two-level system, and the corresponding energy eigenvalues

eigenstates of \( \hat{\sigma}_z = |1\rangle\langle 1| - |2\rangle\langle 2| \)

Boltzmann constant

thermodynamic beta, defined by \( \beta = \frac{1}{k_B T} \)

amplitude, angular frequency, and phase shift for the bias control field
Chapter 1

Introduction

In the last 20 years there has been a transition from the detection of quantum phenomena to their precise control in engineered systems – universal quantum computers are one of the primary goals in this endeavour [1–3]. At the heart of quantum computers is the qubit, which is any quantum system with two possible states, also known as a two-level system (TLS) [1, 4]. What separates the qubit from the classical bit is its adherence to quantum dynamics, and in particular, the ability to be in a superposition of states and having its state collapse after measurement. However, this quantum superposition property of the qubit can be lost due to interactions with the surrounding environment in a process called decoherence [5], thus destroying the quantum mechanical properties of the qubit.

The sensitivity of qubits to their surrounding environment is why the theory of open quantum systems is crucial in the development of quantum computers. An open quantum system refers to any quantum system that is coupled to a non-negligible environment, thus affecting the evolution of the quantum system of interest [6]. Of particular interest for quantum computing is the case of the two-level system (qubit) coupled to an environment, which is an extensively studied open quantum system [7, 8]. Furthermore, as long as the two-level system is not strongly coupled to any of the environmental degrees of freedom, then the environment can be approximated as a collection of independent harmonic oscillators which are linearly coupled to the TLS, which is commonly known as the spin-boson model [7, 9].

The dynamics of the spin-boson system cannot be solved analytically in most cases, and known numerically exact methods are computationally heavy. Thus, approximate methods are useful for their analysis. This thesis mainly studies a particular dynamical description of the spin-boson model, commonly referred to as the reaction coordinate representation [10–12]. Many of the most common approaches rely on weak-coupling approximations or Markovian dynamical models in general. These methods provide
accurate results in certain regimes, but break down in others. The goal of this thesis is to study detailed quantum dynamics using the reaction coordinate master equation, which is not Markovian and hence allows for backflow from the environment into the system. It further allows for strong coupling between the system and environment, making it valid for a wider parameter range than many other models.

In Chapter 2 of this thesis we present the background theoretical framework used throughout. This includes brief introductions to the density operator formalism, open quantum systems, relaxation and dephasing rates, as well as Markovian and non-Markovian dynamics. The chapter ends with sections on the spin-boson model and the reaction coordinate description of it. Chapter 3 begins by introducing a reaction coordinate master equation with a time-independent Hamiltonian, and continues in the following section with a full derivation of the same master equation in the case of a time-dependent TLS.

In Chapter 4 we inspect numerical results in the superconducting qubit regime. We begin with an analysis of the positivity of the reaction coordinate master equation for parameters in the range of interest for our purposes. Next we present a Markovian master equation for the spin-boson model and compare its dynamics to the reaction coordinate master equation. We end the chapter by looking at modelled relaxation and dephasing rates, and see how the reaction coordinate model and Markovian model compare to a real-world measurement. We also test how a time-dependent bias term in the TLS affects the decay rates.

Finally, in Chapter 5 we summarize the results of this thesis, and discuss possible applications for the reaction coordinate master equation.
Chapter 2

Theoretical background

In this chapter, we introduce the background theory for the topics covered in this thesis. First, the basics of open quantum systems and density operators are covered, as they are fundamental concepts in this thesis. Following this we dig deeper into the topic of this work in three separate sections: non-Markovian dynamics of open quantum systems is explained through the trace distance of states criterion [13], the spin-boson model is discussed in connection with a two-level system arising from a double-well approximation [7], and the reaction coordinate is introduced in the context of the spin-boson model.

2.1 Density operator formalism

In the usual pure-state formalism of quantum mechanics, quantum states are associated with unit-norm vectors called ‘kets’, denoted by $|\psi\rangle$, which belong to a Hilbert space of states $H$. However, pure states are unable to describe classical probabilistic mixtures of quantum states. For example, if we have a machine that fires electrons either in a spin up state $|\uparrow\rangle$ or a spin down state $|\downarrow\rangle$ with probabilities $p$ and $(1 - p)$, respectively, then we may be tempted to describe any given state that the machine outputs by

$$|\psi\rangle = \sqrt{p}|\uparrow\rangle + \sqrt{1-p}|\downarrow\rangle.$$

(2.1)

This is wrong, however, as it describes a superposition of the ‘up’ and ‘down’ states rather than a classical mixture.

The density operator is a more general way to model quantum states because it allows for classical mixtures of quantum states in addition to pure states. We define the density operator to be a linear operator from the Hilbert space of states to itself,
written mathematically as
\[ \hat{\rho} : \mathcal{H} \to \mathcal{H}. \] (2.2)

It can be written as a convex combination of a collection of pure states \( \{ |\psi_k\rangle \}_{k=1}^{n} \) expressed in ket-bra form as
\[ \hat{\rho} = \sum_{k=1}^{n} p_k |\psi_k\rangle\langle\psi_k|, \] (2.3)

where the real and positive coefficients \( \{p_k\}_{k=1}^{n} \) obey the condition \( \sum_{k} p_k = 1 \).

Such density operators have the following properties:

(Hermiticity) \[ \hat{\rho}^\dagger = \hat{\rho}, \] (2.4)

(Positivity) \[ \hat{\rho} \geq 0, \] (2.5)

(Unit trace) \[ \text{Tr}(\hat{\rho}) = 1, \] (2.6)

(Purity) \[ \text{Tr}(\hat{\rho}^2) \leq 1, \text{ with equality if and only if } \hat{\rho} \text{ is a pure state}. \] (2.7)

The Hermiticity condition guarantees that the density operator has real eigenvalues. An operator \( \hat{O} : \mathcal{H} \to \mathcal{H} \) is said to be positive semi-definite if its eigenvalues are all greater than or equal to zero. Positivity can be equivalently characterized by the condition that for all vectors \( |\psi\rangle \in \mathcal{H} \), we have that \( \langle\psi| \hat{O} |\psi\rangle \geq 0 \), and we denote this by writing \( \hat{O} \geq 0 \). The trace of an operator \( \hat{O} \) is defined as the sum of its eigenvalues, \( \text{Tr}(\hat{O}) = \sum_\ell \lambda_\ell \). Equivalently, the trace can be computed with respect to any orthonormal basis \( \{ |\varphi_\ell\rangle \}_\ell \) of \( \mathcal{H} \) through the equation
\[ \text{Tr}(\hat{O}) = \sum_\ell \langle\varphi_\ell| \hat{O} |\varphi_\ell\rangle, \] (2.8)

which corresponds to taking the sum of the diagonal elements of \( \hat{O} \) with respect to that basis. The purity of a mixed state, denoted by \( \zeta = \text{Tr}(\hat{\rho}^2) \), is a quantity with bounds \( \frac{1}{\dim(\mathcal{H})} \leq \zeta \leq 1 \), where the upper bound corresponds to pure states and the lower bound to completely mixed states. Completely mixed states are proportional to the identity operator, \( \hat{I} \), and hence the mixed state has equal probability of being in any state of a complete set of orthogonal pure states which form a basis for \( \mathcal{H} \).

We return to the earlier example of the machine that fires electrons in spin up and spin down states; using the density matrix formalism outlined above, we can now express the state of any given electron that the machine outputs as
\[ \hat{\rho} = p |\uparrow\rangle\langle\uparrow| + (1 - p) |\downarrow\rangle\langle\downarrow|. \] (2.9)
We see that the purity of this state is given by \( \zeta = p^2 + (1 - p)^2 \), which takes on values of \( \zeta = 1 \) for \( p = 1 \) and \( p = 0 \). These two cases correspond to the machine always outputting electrons in the spin up state, and the spin down state, respectively. The minimum value of \( \zeta = \frac{1}{2} \) is attained when \( p = \frac{1}{2} \), so the state is completely mixed when both the spin up and spin down states are equally probable.

The need for density operators also arises in composite systems, where we consider the joint system consisting of systems A and B, which we can denote by \( A + B \). Each subsystem has an associated Hilbert space of states, denoted by \( \mathcal{H}_A \) and \( \mathcal{H}_B \), and the Hilbert space of the composite system is given by the tensor product \( \mathcal{H}_A \otimes \mathcal{H}_B \). For any orthonormal bases \( \{ |\varphi_k\rangle \}_k \) of \( \mathcal{H}_A \) and \( \{ |\psi_\ell\rangle \}_\ell \) of \( \mathcal{H}_B \), the set of tensor products \( \{ |\varphi_k\rangle \otimes |\psi_\ell\rangle \}_{k,\ell} \) forms an orthonormal basis for \( \mathcal{H}_A \otimes \mathcal{H}_B \).

In the composite system \( A + B \), an arbitrary pure state \( |\Psi\rangle \in \mathcal{H}_A \otimes \mathcal{H}_B \) can be expanded in terms of the above basis as

\[
|\Psi\rangle = \sum_{k,\ell} c_{k,\ell} |\varphi_k\rangle \otimes |\psi_\ell\rangle. \tag{2.10}
\]

Furthermore, by the Schmidt decomposition theorem it is guaranteed that there exist orthonormal sets \( \{ |\varphi'_i\rangle \}_i \subset \mathcal{H}_A \) and \( \{ |\psi'_j\rangle \}_j \subset \mathcal{H}_B \) such that

\[
|\Psi\rangle = \sum_i d_i |\varphi'_i\rangle \otimes |\psi'_i\rangle. \tag{2.11}
\]

Knowing that the system \( A + B \) is in the state \( |\Psi\rangle \), we can extract the state of either subsystem, let us choose A, by using the density operator representation of \( |\Psi\rangle \),

\[
\hat{\rho} = |\Psi\rangle \langle \Psi| = \sum_{i,j} d_i d_j |\varphi'_i\rangle \langle \varphi'_j| \otimes |\psi'_j\rangle \langle \psi'_i|, \tag{2.12}
\]

and the partial trace over the system B,

\[
\hat{\rho}_A = \text{Tr}_B (\hat{\rho}) = \sum_k \left( \hat{I}_A \otimes \langle \phi_k| \right) |\Psi\rangle \langle \Psi| \left( \hat{I}_A \otimes |\phi_k\rangle \right), \tag{2.13}
\]

where \( \{ |\phi_k\rangle \}_k \) is any orthonormal basis of \( \mathcal{H}_B \). The partial trace gives us the reduced density matrix in the form

\[
\hat{\rho}_A = \sum_i |d_i|^2 |\varphi'_i\rangle \langle \varphi'_i|, \tag{2.14}
\]

which we can see is typically a mixed state. That is, density operators are necessary for describing subsystem states.
2.2 Open quantum systems

In practice, all quantum mechanical systems are open systems [6] since no system can be completely isolated from the rest of the universe. Even so, similarly to classical mechanics where we can often ignore friction without significant loss of precision, the assumption of quantum systems being closed holds accurate to a high degree in many situations. In fact, most of all work that make use of quantum theory function under the assumption of systems being closed. However, in some situations the open nature of the system cannot be ignored since the effect of the environment is too significant. Here a more involved theoretical framework is needed.

Before we introduce open quantum systems, we review closed quantum systems, which provides us a useful point of comparison. A closed quantum system $S$ is modelled by a Hilbert space of states $\mathcal{H}_S$ and a Hamiltonian operator $\hat{H}_S$, which dictates the dynamics of the system density operator $\hat{\rho}_S$ through the Liouville–von Neumann equation

$$\frac{d}{dt} \hat{\rho}_S = -\frac{i}{\hbar} \left[ \hat{H}_S, \hat{\rho}_S \right]. \tag{2.15}$$

It can be shown that Eq. (2.15) is a direct consequence of Schrödinger’s equation and Eq. (2.3). Closed quantum systems can be summarized by the schematic in Figure 2.1.

![Figure 2.1: Schematic image of a closed quantum system. Everything external to the system is assumed to not interact with the system.](image)

For open quantum systems, we consider a situation where our system $S$ is coupled to another system $E$, each with their own respective Hilbert spaces of states $\mathcal{H}_S$ and $\mathcal{H}_E$, so that we have a total system $S + E$ with a Hilbert space of states $\mathcal{H}_S \otimes \mathcal{H}_E$. The Hamiltonian of the total system has the form

$$\hat{H} = \hat{H}_S \otimes \hat{I}_E + \hat{I}_S \otimes \hat{H}_E + \hat{H}_I \tag{2.16}$$

where $\hat{H}_S$ and $\hat{H}_E$ describe the systems $S$ and $E$, respectively, and $\hat{H}_I$ describes how the two systems interact. Again, the dynamics of the total system density operator $\hat{\rho}$
are given by the Liouville–von Neumann equation,

\[
\frac{d}{dt} \hat{\rho} = -\frac{i}{\hbar} \left[ \hat{H}, \hat{\rho} \right]. \tag{2.17}
\]

The schematic picture in Figure 2.2 summarizes open quantum systems.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2_2.png}
\caption{Schematic image of an open quantum system interacting with its environment. The environment is treated as another system that interacts with the open system.}
\end{figure}

The dynamical model for open quantum systems is so far identical to the closed quantum system model; we have only changed the system to include the surrounding environment. However, the environment is typically a very large and complicated system that is not possible to model with perfect accuracy, and even if it were possible, the dynamical equation could become too complicated to solve.

Another issue is extracting the state \( \hat{\rho}_S \) of the system of interest from the total system. Our dynamical equation from Eq. (2.17) tells us how the total system evolves, but we typically only want to know how the open system evolves.

We deal with these issues using a variety of mathematical tools. For extracting the state of the system of interest, we can use the partial trace over the environment degrees of freedom, \( \hat{\rho}_S = \text{Tr}_E (\hat{\rho}) \). We also typically assume that the environment is large compared to the system, so that we can make use of statistical tools such as the central limit theorem to describe the environment by its macroscopic properties.

If we apply the partial trace over the environmental degrees of freedom directly onto Eq. (2.17), we arrive at a new dynamical equation for the open system state \( \hat{\rho}_S \) of the form

\[
\frac{d}{dt} \hat{\rho}_S = -\frac{i}{\hbar} \text{Tr}_E \left[ \hat{H}, \hat{\rho} \right], \tag{2.18}
\]

which is called a quantum master equation. A quantum master equation is any
dynamical equation that models the evolution of the reduced density operator $\hat{\rho}_S$, and Eq. (2.18) is one approach to deriving them. Other approaches include the projection operator technique, used in deriving the Nakajima-Zwanzig equation \cite{14, 15}. The nature of the time-evolution under master equations differs from closed quantum systems where the time evolution of the state is unitary. In closed systems, given an initial state $\hat{\rho}(t_0)$ we can express the state at some time $t > t_0$ as

$$\hat{\rho}(t) = \hat{U}(t, t_0)\hat{\rho}(t_0)\hat{U}^\dagger(t, t_0),$$

(2.19)

where $\hat{U}(t, t_0)$ is a unitary time-evolution operator. In open systems, Eq. (2.19) still holds for the total system, but the partial trace over the environment results in an altered evolution map for the reduced state $\hat{\rho}_S$, called a dynamical map. The dynamical map can be written as an operator $\hat{\mathcal{V}}(t, t_0) : \mathcal{H}_S \rightarrow \mathcal{H}_S$ such that

$$\hat{\rho}_S(t) = \hat{\mathcal{V}}(t, t_0)\hat{\rho}_S(t_0) = \text{Tr}_E \left( \hat{U}(t, t_0)\hat{\rho}(t_0)\hat{U}^\dagger(t, t_0) \right),$$

(2.20)

where $\hat{U}(t, t_0)$ is the unitary time-evolution operator of the total system state $\hat{\rho}$. In the general form of Eq. (2.20) it is difficult to characterize the properties of the dynamical map, but in the special case where the initial state is a product state between the system and a fixed environment, $\hat{\rho}(t_0) = \hat{\rho}_S(t_0) \otimes \hat{\rho}_E$, then we can say that the dynamical map is a linear, completely positive, and trace-preserving map \cite{16}.

Valid quantum operations need to satisfy certain restrictions in order to preserve physicality. For density operators, the positivity condition corresponds to requiring probabilities to be non-negative real numbers, and we require for any physical operation to preserve this property. This leads us to the notion of a positive map, which is defined as some linear superoperator $\Phi : \mathcal{B}(\mathcal{H}) \rightarrow \mathcal{B}(\mathcal{H})$ such that for all positive operators $\hat{\rho} \in \mathcal{B}(\mathcal{H})$, the mapped operator $\Phi(\hat{\rho})$ is also positive.

Positivity is not quite sufficient for open systems, however, since it fails to account for the fact that the open system is a subsystem of a larger system. Even if some operation is localized to a subsystem, we need to account for the existence of the larger system. That is, only those positive maps that can be extended to positive maps in larger systems are considered to be valid \cite{17}, and we refer to this property as complete positivity. Completely positive maps can be defined for any open system where the total Hilbert space is given by $\mathcal{H}_S \otimes \mathcal{H}_n$, where $\mathcal{H}_S$ is the open system Hilbert space and $\mathcal{H}_n$ is an environment Hilbert space of dimension $n$. Then, a map $\Phi : \mathcal{B}(\mathcal{H}_S) \rightarrow \mathcal{B}(\mathcal{H}_S)$ is completely positive if the map $\Phi \otimes \hat{I}_n : \mathcal{B}(\mathcal{H}_S \otimes \mathcal{H}_n) \rightarrow \mathcal{B}(\mathcal{H}_S \otimes \mathcal{H}_n)$ is a positive map for all $n \in \mathbb{N}$, where $\hat{I}_n$ is the identity map \cite{6}. 
2.3 Relaxation and dephasing rates

When an open system has a large environment, the system has a tendency to decay, or relax, to an equilibrium state. The relaxation process of a two-level system can be quantified using two quantities, $T_1^{-1}$ and $T_2^{-1}$, which are known as the relaxation rates [18]. The rate $T_1^{-1}$ is often referred to as the spin-lattice or longitudinal relaxation rate, whereas $T_2^{-1}$ is commonly known as the spin-spin or transverse relaxation rate [1,18]. However, in the context of qubits, $T_1$ is typically called the relaxation time whereas $T_2$ is called the coherence time – this is the nomenclature we use in this thesis.

In the reduced density operator $\hat{\rho}_S$, the parameter $T_1^{-1}$ quantifies the rate of decay of the diagonal elements, $\langle \varphi_k | \hat{\rho}_S | \varphi_k \rangle$, whereas $T_2^{-1}$ quantifies the rate of decay of the off-diagonal terms, $\langle \varphi_K | \hat{\rho}_S | \varphi_\ell \rangle$, where $\{|\varphi_i\rangle\}$ is any orthonormal basis for the open system Hilbert space. The relaxation and coherence times always obey the inequality $T_2 \leq 2T_1$, and the deviation from the equality case is described by the pure dephasing time $T_\phi$, defined by the equation [19,20]

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_\phi}.$$ (2.21)

We can phenomenologically characterize the relaxation rates by starting with the Liouville von-Neumann equation and adding a correction term $\ddot{\hat{\rho}}_{\text{S}} \propto \frac{d\hat{\rho}_S}{dt}$, which encompasses all environmental effects and gives us the equation

$$\frac{d}{dt} \hat{\rho}_S(t) = -\frac{i}{\hbar} \left[ \hat{H}_S, \hat{\rho}_S(t) \right] + \hat{\Lambda}(t).$$ (2.22)

With the assumption that in the $\hat{H}_S$ eigenbasis, $\{|i\rangle\}_i$, the rates of change of the matrix components $\rho_{ij}(t) = \langle i | \hat{\rho}(t) | j \rangle$ are proportional to their deviation from their respective equilibrium values $\rho_{ij}(t \to \infty) \equiv \rho_{ij}^{(\text{th})}$, we can write the following equations:

$$\langle i | \hat{\Lambda}(t) | j \rangle = -\frac{\rho_{ij}(t) - \rho_{ij}^{(\text{th})}}{T_{ij}},$$ (2.23)

$$\langle i | \left[ \hat{H}_S, \hat{\rho}_S(t) \right] | j \rangle = (E_i - E_j)\rho_{ij}.$$ (2.24)

We are only considering a two-level system, so we can write the eigenstates of $\hat{H}_S$ as the ground and excited states $|g\rangle$ and $|e\rangle$, respectively. The density matrix can then be expressed with respect to the eigenbasis of the system Hamiltonian for all times as

$$\rho(t) = \begin{pmatrix}
    \rho_{ee}^{(\text{th})} + (\rho_{ee}(0) - \rho_{ee}^{(\text{th})})e^{-t/T_1} & \rho_{eg}(0)e^{-t/T_2} \\
    \rho_{ge}(0)e^{-t/T_2} & 1 - \rho_{ee}^{(\text{th})} + (\rho_{ee}(0) - \rho_{ee}(0))e^{-t/T_1}
\end{pmatrix}. \quad (2.25)$$
It is important to note that Eq. (2.25) is not suitable for modelling the dynamics of an open system; it only approximates the long-time behaviour and ignores the nature of the interactions between the open system and the environment.

### 2.4 Markovian and non-Markovian dynamics

In a classical setting Markovian and non-Markovian dynamics are defined through the Kolmogorov axioms of probability theory, where a process is Markovian if the conditional probability densities of the random variables for the stochastic process satisfy the Markov condition. Stated in simpler terms, a process is said to be Markovian if its future state only depends on its current state, regardless of how the current state was reached. However, due to quantum characteristics such as the non-commutativity of quantum observables and the wave function collapse after projective measurement, quantum probability does not satisfy the Kolmogorov axioms, and hence the classical definition of Markovianity fails [13, 21].

One way to solve this problem and to define the Markovianity of quantum processes is through the trace distance between two initially distinct states $\hat{\rho}_1$ and $\hat{\rho}_2$ [13, 22]. We consider the time-evolution of these states, $\hat{\rho}_1(t)$ and $\hat{\rho}_2(t)$, and track the evolution of the trace distance over time as

$$D(\hat{\rho}_1, \hat{\rho}_2)(t) = \frac{1}{2} \| \hat{\rho}_1(t) - \hat{\rho}_2(t) \|_{tr},$$

where the trace norm is defined for an operator $\hat{A}$ by

$$\| \hat{A} \|_{tr} = \text{Tr} |\hat{A}| = \text{Tr} \sqrt{\hat{A}^\dagger \hat{A}}.$$  

The trace distance gives us a measure for the distinguishability of two states, where a value 0 denotes indistinguishability, and 1 denotes perfect distinguishability. It further has the property that for any completely positive, trace preserving map $\Lambda$, we have

$$D(\Lambda \hat{\rho}_1, \Lambda \hat{\rho}_2) \leq D(\hat{\rho}_1, \hat{\rho}_2).$$

Thus the distinguishability of two quantum states can never increase under such quantum operation.

In the context of Markovianity of open quantum systems, we can interpret a decrease in the distinguishability of two states, $D(\hat{\rho}_1(t), \hat{\rho}_2(t))$, as dissipation from the open system into the environment, and an increase in the distinguishability as a backflow into the open system from the environment due to system–environment cor-
relations. Hence, given that the initial state is a product state, we can define the dynamics to be Markovian if the distinguishability $D(\Lambda \hat{\rho}_1(t), \Lambda \hat{\rho}_2(t))$ is a monotonically decreasing function, and non-Markovian if it is non-monotonic. We can further quantify the degree of non-Markovianity by the amount of backflow, given by the total amount the distinguishability of the two states increases in a given time interval $t \in [0, t_f]$ [13].

The most general Markovian master equation for the reduced density operator $\hat{\rho}_S$ of an $N$-dimensional open system is the Kossakowski–Lindblad equation [6,23], which has the form

$$\frac{d}{dt} \hat{\rho}_S = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}_S] + \sum_{k,\ell=1}^{N^2-1} a_{k,\ell} \left( \hat{L}_k \hat{\rho}_S \hat{L}_\ell^\dagger - \frac{1}{2} \{ \hat{L}_k^\dagger \hat{L}_\ell, \hat{\rho}_S \} \right), \quad (2.29)$$

where the set $\{ \hat{L}_k \}_{k=1}^{N^2}$ is any complete orthonormal basis for the space of operators on the Hilbert space $\mathcal{H}_S$ such that $\hat{L}_{N^2} = \frac{1}{\sqrt{N}} \hat{I}_S$. It should be noted that Eq. (2.29) is phenomenological, that is, the operators $\hat{L}_k$ do not have a clear connection to any particular physical system. This is in contrast to microscopic derivations of master equations, as outlined in Section 2.2. The benefit of the phenomenological approach is that it can guarantee that the density operator remains physical as it evolves, by construction of the master equation, whereas perturbative methods used in microscopic master equations typically produce unphysical dynamics outside of their intended parameter ranges.

### 2.5 Spin-boson model

A well-known open quantum system is the spin-boson model, which consists of a TLS coupled to a reservoir of bosons. The reservoir can be described by a collection of non-interacting quantum harmonic oscillators [24].

The Hamiltonian of the spin-boson system is given by

$$\hat{H} = \frac{\varepsilon}{2} \hat{\sigma}_z + \frac{\hbar \Delta}{2} \hat{\sigma}_x + \sum_k f_k (\hat{c}_k^\dagger + \hat{c}_k) + \sum_k \hbar \nu_k \hat{c}_k^\dagger \hat{c}_k + \text{const.} \quad (2.30)$$

The constant term at the end of this Hamiltonian refers to any terms that are proportional to the identity operator. They can be ignored for the purposes of studying the system dynamics since $[\hat{I}, \hat{\rho}] = 0$, and hence they vanish in the commutator term of Eq. (2.18).

The TLS portion of the Hamiltonian in Eq. (2.30) can be visualized with a diagram
CHAPTER 2. THEORETICAL BACKGROUND

Figure 2.3: Schematic diagram of the spin-boson model. A TLS is coupled to a bosonic bath where the bosons do not interact with each other.

Based on one from Ref. [7], shown in Figure 2.4.

Figure 2.4: Double-well in two-state limit visualization of a TLS.

As shown in Figure 2.4, the bias term $\varepsilon$ represents the difference in ground state energies within the two potential wells, whereas the tunnelling term $\Delta$ represents the rate of tunnelling between the two wells. It is assumed that $\hbar \Delta \ll \min(\hbar \omega_- , \hbar \omega_+ )$, so that there is virtually no possibility of mixing between the ground states and the excited states of the two wells.

With this interpretation, a result of $-1$ after measuring the $\hat{\sigma}_z$ observable means that the system is localized in the left well, whereas a result of $+1$ means that it is localized in the right well.

The bosonic bath is described through the bosonic creation and annihilation operators, $\hat{c}_k^\dagger$ and $\hat{c}_k$, respectively. The k-th boson has a frequency $\nu_k$, and since $\hat{n}_k = \hat{c}_k^\dagger \hat{c}_k$ is the number operator, the sum $\sum_k \hbar \nu_k \hat{c}_k^\dagger \hat{c}_k$ counts the total energy of the bosons.

Finally, $f_k$ gives the coupling strength between the TLS and the k-th boson in the
bath, which has position \( \hat{x}_k = \sqrt{\hbar/2\nu_k}(\hat{c}_k^\dagger + \hat{c}_k) \) and momentum \( \hat{p}_k = i\sqrt{\hbar\nu_k/2}(\hat{c}_k^\dagger - \hat{c}_k) \), where we have set the boson masses to unity. We assume in the interaction term of the Hamiltonian that the environment couples to the TLS through the \( \hat{\sigma}_z \) operator, which holds true in most real-world systems [7]. This coupling essentially means that the environment is primarily sensitive to which well the TLS is in, using again the double-well interpretation of the TLS.

Since we are typically not interested in the dynamics of the environment, a useful way to simplify the description of the system is to introduce the spectral density [9,12],

\[
J_{SB}(\nu) = \sum_k f_k^2 \delta(\nu - \nu_k),
\]

which completely describes the system-bath interaction. Furthermore, the spectral density for a quantum system can be determined from the semiclassical equation of motion for the system [12], which will be important in the next section.

### 2.6 Reaction coordinate

The idea of the reaction coordinate (RC) is to reduce environmental effects into a single collective coordinate that couples to the quantum system of interest. By doing this, the quantum system of interest is now interacting with another quantum system, the reaction coordinate, which is able to provide indirect feedback between the system of interest and the environment. This allows for the development of a master equation that can track the system-environment correlations [10].

Our goal is to apply the reaction coordinate to the spin-boson model, so our starting point is a TLS coupled to a bosonic bath. We apply a reaction coordinate mapping to the spin-boson model so that the transformed system has the TLS coupled to the RC, which in turn is coupled to a residual bosonic bath [10,11]. The reaction coordinate itself is modelled as a quantum harmonic oscillator. Figure 2.5 shows a schematic diagram of this modified system.

The Hamiltonian after the reaction coordinate mapping is given by

\[
\hat{H}_{RC} = \frac{\epsilon}{2} \hat{\sigma}_z + \frac{\hbar}{2} \hat{\sigma}_x + \lambda \hat{\sigma}_z (\hat{a}^\dagger + \hat{a}) + \frac{\hbar\Omega}{\omega} \hat{\sigma}_x \\
+ \sum_k \hbar \omega_k \hat{b}_k^\dagger \hat{b}_k + (\hat{a}^\dagger + \hat{a}) \sum_k g_k (\hat{b}_k^\dagger + \hat{b}_k) + (\hat{a}^\dagger + \hat{a})^2 \sum_k \frac{g_k^2}{\omega_k},
\]

which represents the Hamiltonian of the modified system.
Figure 2.5: Reaction coordinate schematic diagram. The TLS is coupled to a reaction coordinate, a quantum harmonic oscillator, which is itself coupled to a residual bosonic bath.

where $\hat{a}^\dagger, \hat{a}$ are the ladder operators of the quantum harmonic oscillator (RC), $\lambda$ is the coupling strength between the TLS and the RC, $\Omega$ is the frequency of the RC, $\hat{b}^\dagger_k, \hat{b}_k$ are the creation and annihilation operators of the residual bosonic bath, where the bosons have frequencies $\omega_k$ and coupling strengths $g_k$ with the RC.

The above reaction coordinate quantities are related to the original spin-boson Hamiltonian quantities by the following relations [10,25]:

$$\lambda(\hat{a}^\dagger + \hat{a}) = \sum_k f_k (\hat{c}^\dagger_k + \hat{c}_k),$$  \hspace{1cm} (2.33)

$$\lambda^2 = \sum_k f_k^2,$$  \hspace{1cm} (2.34)

$$\Omega^2 = \frac{\lambda^2}{\sum_k \frac{f_k^2}{\nu_k^2}}.$$  \hspace{1cm} (2.35)

The counter term in Eq. (2.32) corrects for the shift of the physical frequencies of the RC due to the interaction with the residual bath [6,11,26]. The system–bath coupling acts only between the RC and the residual bath, and is again characterized by a spectral density

$$J_{RC}(\omega) = \sum_k g_k^2 \delta(\omega - \omega_k).$$  \hspace{1cm} (2.36)

However, in order to model the dynamics of the spin-boson system we have to find a way to relate the reaction coordinate spectral density $J_{RC}(\omega)$ to the spin-boson spectral density $J_{SB}(\nu)$. As was previously mentioned, the spectral densities for a quantum system are identical to the ones appearing in the corresponding semiclassical equations of motion for the system. After the classical equations of motions have been
2.6. REACTION COORDINATE

found, such that the TLS is associated with a coordinate \( q \) in a potential \( V(q) \), the Fourier transform \( \mathcal{F}[h(t)](z) = \hat{h}(z) = \int_{-\infty}^{\infty} h(t)e^{-izt} \, dt \) is applied to the equations of motion to arrive at an expression of the form

\[
\tilde{K}(z)\tilde{q}(z) = -\tilde{V}'(q),
\]

(2.37)

for both the spin-boson model and the reaction coordinate representation. In both cases we can identify \( J_{SB}(\omega) \) by

\[
J_{SB}(\omega) = \frac{1}{\pi} \lim_{\epsilon \to 0^+} \text{Im} \left[ \tilde{K}(\omega - i\epsilon) \right].
\]

(2.38)

This is commonly referred to as the Leggett prescription [10–12,27].

For the semiclassical equations corresponding to the RC representation, we note that for a damped particle which obeys the Langevin equation, where damping is proportional to the velocity of the particle, the corresponding spectral density is Ohmic [12,28,29]. It can be shown that for an Ohmic spectral density with exponential cutoff frequency \( \Lambda \), defined as

\[
J_{RC}(\omega) = \gamma \omega e^{-\omega/\Lambda},
\]

(2.39)

which describes the interaction between the RC and the residual bath, where \( \gamma \) is the dimensionless coupling strength. The RC classical equations of motion give us the following expression for \( \tilde{K}(z) \) [12]:

\[
\tilde{K}(z) = -z^2 + \frac{\kappa^2}{\Omega^2} \frac{L(z)}{\Omega^2 + L(z)},
\]

(2.40)

where \( \kappa = \sqrt{2}\Omega\lambda \), and \( L(z) \) is defined as

\[
L(z) = -z^2 \left( 1 + 4\Omega \int_{0}^{\infty} \frac{J_{RC}(\omega)}{\omega(\omega^2 - z^2)} \, d\omega \right).
\]

(2.41)

Taking the limit \( \Lambda \to \infty \) allows us to compute the integral in Eq. (2.41), and then by Eq. (2.38) we obtain the spin-boson spectral density

\[
J_{SB}(\omega) = \frac{4\gamma \omega \Omega^2 \lambda^2}{(\Omega^2 - \omega^2)^2 + (2\pi \Omega \gamma)^2 \omega^2}.
\]

(2.42)

The dimensionless coupling strength between the TLS and the bosonic bath is given
by $\alpha$, which is defined as [30]

$$\alpha = \lim_{\omega \to 0^+} \frac{J_{SB}(\omega)}{2\omega} = \frac{2\gamma \lambda^2}{\Omega^2}. \quad (2.43)$$

Refer to Appendix A for a full computation of the spectral density $J_{SB}(\omega)$. 


Chapter 3

Reaction coordinate master equation

The reaction coordinate representation of the spin-boson model has been used for various applications, such as modelling biomolecules, solid-state devices, electron-transfer reactions, and likely many others [10–12, 25]. Although the reaction coordinate mapping is the same in all implementations, the dynamical equations describing the systems often differ due to differences in approximations used. The main allure of the reaction coordinate approach is that it provides a straightforward way to model non-Markovian dynamics for a wide variety of systems. In this chapter we summarize the main results of Ref. [10], and then follow their methodology to derive a reaction coordinate master equation with a time-dependent TLS, showing that it has the same form as in the time-independent case.

3.1 Time-independent Hamiltonian

The reaction coordinate approach has been used in previous work [10] to obtain a master equation for a spin-boson system that holds for low temperatures and strong coupling strength, given by

$$\frac{\partial \hat{\rho}(t)}{\partial t} = -\frac{i}{\hbar} [\hat{H}_0, \hat{\rho}(t)] - \frac{1}{\hbar} [\hat{A}, [\hat{\chi}, \hat{\rho}(t)]] + \frac{1}{\hbar^2} [\hat{A}, \{\hat{\Xi}, \hat{\rho}(t)\}],$$  \hspace{1cm} (3.1)

where $\hat{A} = \hat{a}^\dagger + \hat{a}$ is proportional to the position operator of the reaction coordinate, and $\hat{H}_0 = \frac{\epsilon}{2} \hat{\sigma}_z + \frac{\hbar \Delta}{2} \hat{\sigma}_x + \lambda \hat{\sigma}_z (\hat{a}^\dagger + \hat{a}) + \hbar \Omega \hat{a}^\dagger \hat{a}$ is the TLS–RC Hamiltonian. The operators $\hat{\chi}$ and $\hat{\Xi}$ characterize the effect of the RC–bath coupling on the evolution of the system, and are defined as
\[
\hat{\chi} = \int_0^\infty \int_0^\infty d\tau d\omega J_{\text{RC}}(\omega) \cos(\omega t) \coth\left(\frac{\beta \hbar \omega}{2}\right) \hat{A}_I(-\tau), \quad (3.2)
\]

\[
\hat{\Xi} = \int_0^\infty \int_0^\infty d\tau d\omega J_{\text{RC}}(\omega) \cos(\omega \tau) \frac{\omega}{\hat{H}_0, \hat{A}_I(-\tau)}, \quad (3.3)
\]

where \(\hat{A}_I(t) = e^{i\hat{H}_0 t/\hbar} \hat{A} e^{-i\hat{H}_0 t/\hbar}\) is the interaction picture representation of \(\hat{A}\), and \(J_{\text{RC}}(\omega) = \gamma \omega\) is the Ohmic spectral density in the RC representation with infinite exponential cutoff frequency, as explained in Section 2.6.

Numerical results of Eq. (3.1) are investigated in Refs. [10,11], showing significant deviations from a Markovian master equation as well as strong agreement with the hierarchical equations of motion, a particularly accurate yet computationally demanding method [31].

### 3.2 Time-dependent two-level system

Let us consider a situation where the parameters \(\epsilon\) and \(\Delta\) of the TLS are time-dependent functions \(\epsilon(t), \Delta(t)\). Thus the Hamiltonian \(\hat{H}_0\) in Eq. (3.1) is no longer time-independent, and hence the interaction picture representation of \(\hat{A}\) can no longer be expressed as \(\hat{A}_I(t) = e^{i\hat{H}_0 t/\hbar} \hat{A} e^{-i\hat{H}_0 t/\hbar}\), but instead in the general form

\[
\hat{A}_I(t) = \hat{U}(t) \hat{A} \hat{U}(t)^\dagger, \quad (3.4)
\]

where \(\hat{U}(t)\) is the time evolution operator corresponding to the time-dependent Hamiltonian \(H_0(t)\). It can be shown that

\[
[H_0(t), H_0(t')] = 2\hbar i \sigma_y \otimes \left[ \frac{1}{4} \det \begin{pmatrix} \epsilon(t) & \Delta(t) \\ \epsilon(t') & \Delta(t') \end{pmatrix} \hat{I}_{\text{RC}} - \frac{\lambda}{2} (\Delta(t') - \Delta(t)) (\hat{a}^\dagger + \hat{a}) \right],
\]

which vanishes only if \(\det \begin{pmatrix} \epsilon(t) & \Delta(t) \\ \epsilon(t') & \Delta(t') \end{pmatrix} = 0\) and either \(\Delta(t') = \Delta(t)\) or \(\lambda = 0\). This is equivalent to requiring that \((\epsilon(t), \Delta(t)) = (\epsilon(t'), \Delta(t'))\) for all \(t, t' \in \mathbb{R}\), or having \(\Delta(t) = 0\) for all \(t \in \mathbb{R}\). This means that any non-trivial time dependence of \(\epsilon\) or \(\Delta\) will break the commutativity of the Hamiltonian at different times. Consequently the
3.2. TIME-DEPENDENT TWO-LEVEL SYSTEM

The time evolution operator assumes the form

\[ \hat{U}(t) = T \left\{ \exp \left( -i \frac{\hbar}{\hbar} \int_0^t \hat{H}_0(t') \, dt' \right) \right\}, \]  

(3.6)

where we have introduced the Dyson series formulation which includes the time-ordering operator \( T \).

Another possible complication is that the derivation of the RC master equation in Ref. [10] assumes that the reaction coordinate Hamiltonian is time-independent, and hence it is not guaranteed that the existing master equation in Eq. 3.1 holds true in the case of a time-dependent TLS. The following section of this chapter addresses this concern.

3.2.1 Master equation for time-dependent control

In this section, we present a full derivation of a master equation for the RC representation of the spin-boson model, with the assumption that the TLS portion of the Hamiltonian, \( \hat{H}_{\text{TLS}} \), has a time dependence of the form

\[ \hat{H}_{\text{TLS}}(t) = \frac{\varepsilon(t)}{2} \hat{\sigma}_z + \frac{\hbar \Delta(t)}{2} \hat{\sigma}_x. \]  

(3.7)

We mostly follow the methods outlined in Ref. [10]. The RC Hamiltonian in the Schrödinger picture has the form

\[ \hat{H}_{\text{RC,S}} = \frac{\varepsilon(t)}{2} \hat{\sigma}_z + \frac{\hbar \Delta(t)}{2} \hat{\sigma}_x + \lambda \hat{\sigma}_z (\hat{a}^\dagger + \hat{a}) + \hbar \Omega \hat{a}^\dagger \hat{a} \] 
\[ \begin{align*} &+ \sum_k \hbar \omega_k \hat{b}^\dagger_k \hat{b}_k + (\hat{a}^\dagger + \hat{a}) \sum_k g_k (\hat{b}_k^\dagger + \hat{b}_k) + (\hat{a}^\dagger + \hat{a})^2 \sum_k \frac{g_k^2}{\hbar \omega_k} \end{align*} \]  

(3.8)

\[ \begin{align*} &+ \sum_k \hbar \omega_k \hat{b}_k^\dagger \hat{b}_k, \quad \hat{H}_B = \sum_k \hbar \omega_k \hat{b}_k^\dagger \hat{b}_k, \quad \hat{H}_{1,S} = \frac{\varepsilon(t)}{2} \hat{\sigma}_z + \frac{\hbar \Delta(t)}{2} \hat{\sigma}_x + (\hat{a}^\dagger + \hat{a}) \sum_k g_k (\hat{b}_k^\dagger + \hat{b}_k) + (\hat{a}^\dagger + \hat{a})^2 \sum_k \frac{g_k^2}{\hbar \omega_k} \end{align*} \]  

(3.9)

where the components are given by

\[ \begin{align*} \hat{H}_{0,S} &= \lambda \hat{\sigma}_z (\hat{a}^\dagger + \hat{a}) + \hbar \Omega \hat{a}^\dagger \hat{a}, \quad \hat{H}_{1,S} = \frac{\varepsilon(t)}{2} \hat{\sigma}_z + \frac{\hbar \Delta(t)}{2} \hat{\sigma}_x + (\hat{a}^\dagger + \hat{a}) \sum_k g_k (\hat{b}_k^\dagger + \hat{b}_k) + (\hat{a}^\dagger + \hat{a})^2 \sum_k \frac{g_k^2}{\hbar \omega_k} \end{align*} \]  

(3.10)
We introduce the following operators for brevity,

\[ \hat{T}_S(t) = \frac{\varepsilon(t)}{2} \hat{\sigma}_z + \frac{\hbar \Delta(t)}{2} \hat{\sigma}_x, \quad (3.14) \]

\[ \hat{A}_S = \hat{a}^\dagger + \hat{a}, \quad (3.15) \]

\[ \hat{B}_S = \sum_k g_k (\hat{b}_k^\dagger + \hat{b}_k), \quad (3.16) \]

\[ \tilde{\lambda} = \sum_k g_k^2 \hbar \omega_k. \quad (3.17) \]

Thus we can express \( \hat{H}_{1,S} \) as

\[ \hat{H}_{1,S} = \hat{T}_S(t) \otimes \hat{I}_{RC} \otimes \hat{I}_B + \hat{I}_{TLS} \otimes \hat{A}_S \otimes \hat{B}_S + \hat{I}_{TLS} \otimes \tilde{\lambda} \hat{A}_S^2 \otimes \hat{I}_B. \quad (3.18) \]

We have included the tensor products explicitly in Eq. (3.18), and in the computations that follow, in order to improve readability. Below, we employ the interaction picture with respect to \( \hat{H}_{0,S} + \hat{H}_B \) where \( \hat{H}_{1,S} \) transforms into \( \hat{H}_{1,I} \) and has the form

\[ \hat{H}_{1,I}(t) = e^{\frac{i}{\hbar} (\hat{H}_{0,S} + \hat{H}_B) t} \hat{H}_{1,S} e^{-\frac{i}{\hbar} (\hat{H}_{0,S} + \hat{H}_B) t} = \hat{T}_I(t) \otimes \hat{I}_{RC} \otimes \hat{I}_B + \hat{I}_{TLS} \otimes \hat{A}_I(t) \otimes \hat{B}_I(t) + \hat{I}_{TLS} \otimes \tilde{\lambda} \hat{A}_I^2(t) \otimes \hat{I}_B. \quad (3.19) \]

Furthermore, the von Neumann equation for the evolution of the density operator \( \hat{\rho}_I \) in the interaction picture is given by

\[ \frac{\partial \hat{\rho}_I(t)}{\partial t} = -\frac{i}{\hbar} \left[ \hat{H}_{1,I}(t), \hat{\rho}_I(t) \right], \quad (3.21) \]

which has an integral form where we assume an initial time of \( t_0 = 0 \), and hence it can be written as

\[ \hat{\rho}_I(t) = \hat{\rho}_I(0) - \frac{i}{\hbar} \int_0^t d\tau \left[ \hat{H}_{1,I}(\tau), \hat{\rho}_I(\tau) \right]. \quad (3.22) \]

By inserting on the right side of Eq. (3.21) the integral form of the von Neumann equation in Eq. (3.22) and tracing out the bath, we obtain

\[ \frac{\partial \hat{\rho}_{sys,I}(t)}{\partial t} = -\frac{i}{\hbar} \text{Tr}_B \left\{ \left[ \hat{H}_{1,I}(t), \hat{\rho}_I(0) \right] \right\} - \frac{1}{\hbar^2} \int_0^t d\tau \text{Tr}_B \left\{ \left[ \hat{H}_{1,I}(\tau), \left[ \hat{H}_{1,I}(\tau), \hat{\rho}_I(\tau) \right] \right] \right\}, \quad (3.23) \]

where \( \hat{\rho}_{sys,I}(t) = \text{Tr}_B [\hat{\rho}_I(t)] \). At this point we make the Born approximation, and assume that \( \hat{\rho}_I(t) = \hat{\rho}_{sys,I}(t) \otimes \hat{\rho}_B,I \) for all times \( t \), where \( \hat{\rho}_B = e^{-\beta \sum \omega_k b_k^\dagger b_k} / \text{Tr} \left( e^{-\beta \sum \omega_k b_k^\dagger b_k} \right) \) is the density operator for the residual bath, describing a thermal equilibrium state.
Thus, Eq. (3.23) becomes

\[
\frac{\partial \rho_{\text{sys},1}(t)}{\partial t} = -\frac{i}{\hbar} \text{Tr}_B \left[ \hat{H}_{1,1}(t), \hat{\rho}_{\text{sys},1}(0) \otimes \hat{\rho}_{B,1} \right] - \frac{1}{\hbar^2} \int_0^t d\tau \text{Tr}_B \left[ \hat{H}_{1,1}(\tau), \left[ \hat{H}_{1,1}(\tau), \hat{\rho}_{\text{sys},1}(\tau) \otimes \hat{\rho}_{B,1} \right] \right].
\] (3.24)

We first note that the first line in Eq. (3.24) expands to

\[
\text{Tr}_B \left\{ \left[ \hat{H}_{1,1}(t), \hat{\rho}_{\text{sys},1}(0) \otimes \hat{\rho}_{B,1} \right] \right\} = \text{Tr}_B \left\{ \left[ \hat{T}_I(t) \otimes \hat{I}_{\text{RC}} \otimes \hat{I}_{B} \hat{\rho}_{\text{sys},1}(0) \otimes \hat{\rho}_{B,1} \right] \right\} + \text{Tr}_B \left\{ \left[ \hat{I}_{\text{TLS}} \otimes \hat{A}_1(t) \otimes \hat{B}_1(t), \hat{\rho}_{\text{sys},1}(0) \otimes \hat{\rho}_{B,1} \right] \right\} + \text{Tr}_B \left\{ \left[ \hat{I}_{\text{TLS}} \otimes \hat{\lambda}_1^2(t) \otimes \hat{I}_{B}, \hat{\rho}_{\text{sys},1}(0) \otimes \hat{\rho}_{B,1} \right] \right\} ,
\] (3.25)

where it can be shown that the term on the second line is zero, so that Eq. (3.25) simplifies to

\[
\text{Tr}_B \left\{ \left[ \hat{H}_{1,1}(t), \hat{\rho}_{\text{sys},1}(0) \otimes \hat{\rho}_{B,1} \right] \right\} = \text{Tr}_B \left\{ \left[ \hat{T}_I(t) \otimes \hat{I}_{\text{RC}} \otimes \hat{I}_{B} \hat{\rho}_{\text{sys},1}(0) \otimes \hat{\rho}_{B,1} \right] \right\}.
\] (3.26)

To match the above form, we expand out the Hamiltonian \( \hat{H}_{1,1}(t) \) in the second line of Eq. (3.24) and split it into two parts as follows

\[
\text{Tr}_B \left\{ \left[ \hat{H}_{1,1}(t), \left[ \hat{H}_{1,1}(\tau), \hat{\rho}_{\text{sys},1}(\tau) \otimes \hat{\rho}_{B,1} \right] \right] \right\} = \text{Tr}_B \left\{ \left[ \hat{T}_I(t) \otimes \hat{I}_{\text{RC}} \otimes \hat{I}_{B} \hat{\rho}_{\text{sys},1}(0) \otimes \hat{\rho}_{B,1} \right] \right\} + \text{Tr}_B \left\{ \left[ \hat{I}_{\text{TLS}} \otimes \hat{A}_1(t) \otimes \hat{B}_1(t), \left[ \hat{H}_{1,1}(\tau), \hat{\rho}_{\text{sys},1}(\tau) \otimes \hat{\rho}_{B,1} \right] \right] \right\}.
\] (3.27)

Notice that we were able to move the partial trace inside the commutator in the second line because the Hamiltonian components on the left side of the outer commutator are proportional to the identity operator on the bath Hilbert space.

The master equation can now be written as

\[
\frac{\partial \rho_{\text{sys},1}(t)}{\partial t} = -\frac{i}{\hbar} \text{Tr}_B \left\{ \left[ \hat{T}_I(t) \otimes \hat{I}_{\text{RC}} \otimes \hat{I}_{B} \hat{\rho}_{\text{sys},1}(0) \otimes \hat{\rho}_{B,1} \right] \right\} - \frac{1}{\hbar^2} \int_0^t d\tau \text{Tr}_B \left\{ \left[ \hat{T}_I(t) \otimes \hat{I}_{\text{RC}} \otimes \hat{I}_{B} + \hat{I}_{\text{TLS}} \otimes \hat{\lambda}_1^2(t) \otimes \hat{I}_{B}, \hat{\rho}_{\text{sys},1}(0) \otimes \hat{\rho}_{B,1} \right] \right\} - \frac{1}{\hbar^2} \int_0^t d\tau \text{Tr}_B \left\{ \left[ \hat{I}_{\text{TLS}} \otimes \hat{A}_1(t) \otimes \hat{B}_1(t), \left[ \hat{H}_{1,1}(\tau), \hat{\rho}_{\text{sys},1}(\tau) \otimes \hat{\rho}_{B,1} \right] \right] \right\}.
\] (3.28)
The first two lines of Eq. (3.28) can be simplified by bringing the integral term
\(-i/\hbar \int_0^t d\tau\) into the commutator on the second line, and then combining the first
two lines by linearity to give

\[
- \frac{i}{\hbar} \text{Tr}_B \left\{ \left[ \hat{T}_I(t) \otimes \hat{\lambda} \hat{A}_I^2(t) \otimes \hat{I}_B, \hat{\rho}_{\text{sys},1}(0) \otimes \hat{\rho}_{B,1} \right] \right\}
- \frac{1}{\hbar^2} \int_0^t d\tau \left[ \hat{T}_I(t) \otimes \hat{I}_B + \hat{I}_{\text{TLS}} \otimes \hat{\lambda} \hat{A}_I^2(t) \otimes \hat{I}_B, \text{Tr}_B \left\{ \left[ \hat{H}_{1,1}(\tau), \hat{\rho}_{\text{sys},1}(\tau) \otimes \hat{\rho}_{B,1} \right] \right\} \right]
= - \frac{i}{\hbar} \text{Tr}_B \left\{ \left[ \hat{T}_I(t) \otimes \hat{\lambda} \hat{A}_I^2(t) \otimes \hat{I}_B, \hat{\rho}_{\text{sys},1}(0) \otimes \hat{\rho}_{B,1} \right] \right\}
= - \frac{i}{\hbar} \left( \hat{T}_I(t) \otimes \hat{\lambda} \hat{A}_I(t) \right) + \hat{\lambda} \left[ \hat{I}_{\text{TLS}} \otimes \hat{A}_I^2(t), \hat{\rho}_{\text{sys},1}(t) \right].
\tag{3.29}
\]

In the second last equality in Eq. (3.29) we used the von Neumann equation from
Eq. (3.22) to arrive at the final result.

We are left with simplifying the last line of Eq. (3.28), which we can start by
expanding the trace within the integral,

\[
\text{Tr}_B \left\{ \left[ \hat{I}_{\text{TLS}} \otimes \hat{A}_I(t) \otimes \hat{B}_I(t), \left[ \hat{H}_{1,1}(\tau), \hat{\rho}_{\text{sys},1}(\tau) \otimes \hat{\rho}_{B,1} \right] \right] \right\}
\tag{3.30}
= \text{Tr}_B \left[ \hat{I}_{\text{TLS}} \otimes \hat{A}_I(t) \otimes \hat{B}_I(t), \left[ \hat{T}_I(\tau) \otimes \hat{I}_B, \hat{\rho}_{\text{sys},1}(\tau) \otimes \hat{\rho}_{B,1} \right] \right]
+ \text{Tr}_B \left[ \hat{I}_{\text{TLS}} \otimes \hat{A}_I(t) \otimes \hat{B}_I(t), \hat{I}_{\text{TLS}} \otimes \hat{\lambda} \hat{A}_I^2(\tau) \otimes \hat{I}_B, \hat{\rho}_{\text{sys},1}(\tau) \otimes \hat{\rho}_{B,1} \right]
+ \text{Tr}_B \left[ \hat{I}_{\text{TLS}} \otimes \hat{A}_I(t) \otimes \hat{B}_I(t), \hat{I}_{\text{TLS}} \otimes \hat{\lambda} \hat{A}_I^2(\tau) \otimes \hat{I}_B, \hat{\rho}_{\text{sys},1}(\tau) \otimes \hat{\rho}_{B,1} \right].
\tag{3.31}
\]

It can be shown that the first and last terms of the expanded form for the above
trace are proportional to the bath expectation value, which in Appendix C is shown
to vanish, so that

\[
\left< \hat{B}_I(t) \right>_{\hat{\rho}_n} = 0.
\tag{3.34}
\]

We are now left with only the RC-Bath interaction terms of the Hamiltonian within
the integral, and the master equation is thus given by

\[
\frac{\partial \hat{\rho}_{\text{sys},1}(t)}{\partial t} = - \frac{i}{\hbar} \left( \left[ \hat{T}_I(t) \otimes \hat{\lambda} \hat{A}_I^2(t), \hat{\rho}_{\text{sys},1}(t) \right] \right) + \hat{\lambda} \left[ \hat{I}_{\text{TLS}} \otimes \hat{A}_I^2(t), \hat{\rho}_{\text{sys},1}(t) \right],
\]

\[
- \frac{1}{\hbar^2} \int_0^t d\tau \text{Tr}_B \left\{ \left[ \hat{I}_{\text{TLS}} \otimes \hat{A}_I(t) \otimes \hat{B}_I(t), \hat{I}_{\text{TLS}} \otimes \hat{A}_I(\tau) \otimes \hat{B}_I(\tau), \hat{\rho}_{\text{sys},1}(\tau) \otimes \hat{\rho}_{B,1} \right] \right\}. \tag{3.35}
\]
To simplify the integral in Eq. (3.35) we apply the Markov approximation, so that feedback from the bath to the reaction coordinate is ignored. This can be done by first replacing \( \rho_{\text{sys},1}(\tau) \) with \( \rho_{\text{sys},1}(t) \), so the time-evolution of the system does not explicitly depend on its state at earlier times. After this, we can make the substitution \( \tau \rightarrow t - \tau \) which does not affect the integral due to sign cancellation: \( \int_0^\infty d\tau \rightarrow \int_t^0 (-d\tau) \rightarrow \int_0^t d\tau \).

Then, assuming that the integrand decays sufficiently quickly, we can take the limit \( t \rightarrow \infty \) and arrive at the Born-Markov approximation for the master equation, given by

\[
\frac{\partial \rho_{\text{sys},1}(t)}{\partial t} = \frac{-i}{\hbar} \left( \left[ \hat{I}_{\text{TLS}}(t) \otimes \hat{I}_{\text{RC}}, \rho_{\text{sys},1}(t) \right] + \lambda \left[ \hat{I}_{\text{TLS}} \otimes \hat{A}_1^2(t), \rho_{\text{sys},1}(t) \right] \right)
- \frac{1}{\hbar^2} \int_0^\infty d\tau \text{Tr}_B \left\{ \left[ \hat{I}_{\text{TLS}} \otimes \hat{A}_1(t) \otimes \hat{B}_1(t) \right], \left[ \hat{I}_{\text{TLS}} \otimes \hat{A}_1(t - \tau) \otimes \hat{B}_1(t - \tau), \rho_{\text{sys},1}(t) \otimes \hat{\rho}_{\text{B},1} \right] \right\}.
\]

(3.36)

The partial trace within the integral in Eq. (3.36) can be reduced to a sum of two terms involving a trace over bath operators only:

\[
\text{Tr}_B \left[ \hat{I}_{\text{TLS}} \otimes \hat{A}_1(t) \otimes \hat{B}_1(t) \right], \left[ \hat{I}_{\text{TLS}} \otimes \hat{A}_1(t - \tau) \otimes \hat{B}_1(t - \tau), \rho_{\text{sys},1}(t) \otimes \hat{\rho}_{\text{B},1} \right]
= \text{Tr} \left[ \hat{B}_1(t) \hat{B}_1(t - \tau) \hat{\rho}_{\text{B},1} \right] \left[ \hat{A}_1(t) \hat{A}_1(t - \tau) \rho_{\text{sys},1}(t) - \hat{A}_1(t - \tau) \hat{\rho}_{\text{sys},1}(t) \hat{A}_1(t) \right] + \text{Tr} \left[ \hat{B}_1(t - \tau) \hat{B}_1(t) \hat{\rho}_{\text{B},1} \right] \left[ -\hat{A}_1(t) \hat{\rho}_{\text{sys},1}(t) \hat{A}_1(t - \tau) + \hat{\rho}_{\text{sys},1}(t) \hat{A}_1(t - \tau) \hat{A}_1(t) \right].
\]

(3.37)

The TLS identity operator \( \hat{I}_{\text{TLS}} \) has been made implicit on the right-hand side of Eq. (3.37) for better readability. Note that it can be re-introduced by making the replacement \( \hat{A}_1(\bullet) \rightarrow \hat{I}_{\text{TLS}} \otimes \hat{A}_1(\bullet) \), which we shall do later. To deal with the trace terms in Eq. (3.37) we notice that

\[
\hat{B}_1(t) \hat{B}_1(t - \tau) = e^{i\hat{H}_B t} \hat{B} e^{-i\hat{H}_B (t-\tau)} \hat{B} e^{-i\hat{H}_B (t-\tau)}
= e^{i\hat{H}_B t} \hat{B} e^{-i\hat{H}_B t} \hat{B} e^{-i\hat{H}_B t}
= e^{i\hat{H}_B t} \hat{B} \hat{B}_S (-\tau) e^{-i\hat{H}_B t},
\]

(3.38)

where \( \hat{B} = \hat{B}_1(0) = \hat{B}_S \). From Eq. (3.38) coupled with the relation \([\hat{H}_B, \hat{\rho}_{\text{B}}] = 0\) it follows that

\[
\text{Tr} \left[ \hat{B}_1(t) \hat{B}_1(t - \tau) \hat{\rho}_{\text{B},1} \right] = \text{Tr} \left[ e^{i\hat{H}_B t} \hat{B} \hat{B}_S (-\tau) e^{-i\hat{H}_B t} \hat{\rho}_{\text{B},1} \right]
= \text{Tr} \left[ \hat{B} \hat{B}_S (-\tau) \hat{\rho}_{\text{B},1} \right].
\]

(3.39)
Using Eqs. (3.40) and (3.42), the right-hand side of Eq. (3.37) takes on the form so that

\[ \text{Tr} \left[ \hat{B} \hat{B}_1(-\tau) \hat{\rho}_{B,1} \right] = \text{Tr} \left[ \hat{B}_1(\tau) \hat{B} \hat{\rho}_{B,1} \right]. \]  

(3.40)

Similarly, we have

\[ \hat{B}_1(t - \tau) \hat{B}_1(t) = e^{i\hat{H}_B t} \hat{B}_1(-\tau) \hat{B} e^{-i\hat{H}_B t}, \]  

(3.41)

so that

\[ \text{Tr} \left[ \hat{B}_1(t - \tau) \hat{B}_1(t) \hat{\rho}_{B,1} \right] = \text{Tr} \left[ \hat{B}_1(-\tau) \hat{B} \hat{\rho}_{B,1} \right]. \]  

(3.42)

Using Eqs. (3.40) and (3.42), the right-hand side of Eq. (3.37) takes on the form

\[
(3.37) = \frac{1}{2} \text{Tr} \left[ \hat{B}_1(\tau) \hat{B} \hat{\rho}_{B,1} \right] \left[ 2 \hat{A}_1(t) \hat{A}_1(t - \tau) \hat{\rho}_{\text{sys},1}(t) - 2 \hat{A}_1(t - \tau) \hat{\rho}_{\text{sys},1}(t) \hat{A}_1(t) \right] \\
+ \frac{1}{2} \text{Tr} \left[ \hat{B}_1(-\tau) \hat{B} \hat{\rho}_{B,1} \right] \left[ -2 \hat{A}_1(t) \hat{\rho}_{\text{sys},1}(t) \hat{A}_1(t - \tau) + 2 \hat{\rho}_{\text{sys},1}(t) \hat{A}_1(t - \tau) \hat{A}_1(t) \right] \\
= \frac{1}{2} \left\{ \hat{A}_1(t) \left[ \hat{A}_1(t - \tau) \hat{\rho}_{\text{sys},1}(t) - \hat{\rho}_{\text{sys},1}(t) \hat{A}_1(t - \tau) \right] \\
- \left[ \hat{A}_1(t - \tau) \hat{\rho}_{\text{sys},1}(t) - \hat{\rho}_{\text{sys},1}(t) \hat{A}_1(t - \tau) \right] \hat{A}_1(t) \right\} \text{Tr} \left[ \hat{B}_1(\tau) \hat{B} \hat{\rho}_{B,1} \right] \\
+ \frac{1}{2} \left\{ \hat{A}_1(t) \left[ \hat{A}_1(t - \tau) \hat{\rho}_{\text{sys},1}(t) + \hat{\rho}_{\text{sys},1}(t) \hat{A}_1(t - \tau) \right] \\
- \left[ \hat{A}_1(t - \tau) \hat{\rho}_{\text{sys},1}(t) + \hat{\rho}_{\text{sys},1}(t) \hat{A}_1(t - \tau) \right] \hat{A}_1(t) \right\} \text{Tr} \left[ \hat{B}_1(-\tau) \hat{B} \hat{\rho}_{B,1} \right] \\
- \frac{1}{2} \left\{ \hat{A}_1(t) \left[ \hat{A}_1(t - \tau) \hat{\rho}_{\text{sys},1}(t) + \hat{\rho}_{\text{sys},1}(t) \hat{A}_1(t - \tau) \right] \\
- \left[ \hat{A}_1(t - \tau) \hat{\rho}_{\text{sys},1}(t) + \hat{\rho}_{\text{sys},1}(t) \hat{A}_1(t - \tau) \right] \hat{A}_1(t) \right\} \text{Tr} \left[ \hat{B}_1(-\tau) \hat{B} \hat{\rho}_{B,1} \right] \\
= \left[ \hat{A}_1(t), \left[ \hat{A}_1(t - \tau), \hat{\rho}_{\text{sys},1}(t) \right] \right] \frac{1}{2} \text{Tr} \left\{ \left( \hat{B}_1(\tau) \hat{B} + \hat{B}_1(-\tau) \hat{B} \right) \hat{\rho}_{B,1} \right\} \\
+ \left[ \hat{A}_1(t), \left\{ \hat{A}_1(t - \tau), \hat{\rho}_{\text{sys},1}(t) \right\} \right] \frac{1}{2} \text{Tr} \left\{ \left( \hat{B}_1(\tau) \hat{B} - \hat{B}_1(-\tau) \hat{B} \right) \hat{\rho}_{B,1} \right\}. 
\]

Defining the bath correlation functions \( \Gamma^\pm(\tau) \) by

\[ \Gamma^\pm(\tau) = \frac{1}{2} \text{Tr} \left[ \left( \hat{B}_1(\tau) \hat{B} \pm \hat{B}_1(-\tau) \hat{B} \right) \hat{\rho}_{B,1} \right], \]  

(3.43)
Eq. (3.37) may be expressed as

\[
\begin{aligned}
\text{Tr}_B \left[ \hat{A}_1(t) \otimes \hat{B}_1(t), \left[ \hat{A}_1(t - \tau) \otimes \hat{B}_1(t - \tau), \hat{\rho}_{\text{sys},1}(t) \otimes \hat{\rho}_{B,1} \right] \right] \\
= \left[ \hat{A}_1(t), \left[ \hat{A}_1(t - \tau), \hat{\rho}_{\text{sys},1}(t) \right] \right] \Gamma^+(\tau) \\
+ \left[ \hat{A}_1(t), \left\{ \hat{A}_1(t - \tau), \hat{\rho}_{\text{sys},1}(t) \right\} \right] \Gamma^-(\tau).
\end{aligned}
\]  

(3.44)

At this point the master equation has been simplified to

\[
\begin{aligned}
\frac{\partial \hat{\rho}_{\text{sys},1}(t)}{\partial t} &= -\frac{i}{\hbar} \left[ \hat{T}_1(t) \otimes \hat{I}_{RC}, \hat{\rho}_{\text{sys},1}(t) \right] \\
&+ \frac{i}{\hbar} \lambda \left[ \hat{I}_{\text{TLS}} \otimes \hat{\rho}_{\text{sys},1}(t) \right] \\
&- \frac{1}{\hbar^2} \int_0^\infty d\tau \{ \left[ \hat{A}_1(t), \left[ \hat{A}_1(t - \tau), \hat{\rho}_{\text{sys},1}(t) \right] \right] \Gamma^+(\tau) \\
&+ \left[ \hat{A}_1(t), \left\{ \hat{A}_1(t - \tau), \hat{\rho}_{\text{sys},1}(t) \right\} \right] \Gamma^-(\tau) \}.
\end{aligned}
\]  

(3.45)

(3.46)

Taking the continuum limit for the environmental modes, the bath correlation functions assume the forms [6,12,32,33]

\[
\begin{aligned}
\Gamma^+(\tau) &= \hbar \int_0^\infty d\omega J_{RC}(\omega) \coth \left( \frac{\beta \hbar \omega}{2} \right) \cos(\omega \tau), \\
\Gamma^-(\tau) &= -i\hbar \int_0^\infty d\omega J_{RC}(\omega) \sin(\omega \tau).
\end{aligned}
\]  

(3.47)

(3.48)

We note that \( \frac{\hbar \omega}{2} \coth \left( \frac{\beta \hbar \omega}{2} \right) \) is the average energy of the bosonic oscillators with frequency \( \omega \) and temperature \( T = 1/k_B \beta \) [34]. Thus the master equation can be written as

\[
\begin{aligned}
\frac{\partial \hat{\rho}_{\text{sys},1}(t)}{\partial t} &= -\frac{i}{\hbar} \left[ \hat{T}_1(t) \otimes \hat{I}_{RC}, \hat{\rho}_{\text{sys},1}(t) \right] \\
&- \frac{i}{\hbar} \lambda \left[ \hat{I}_{\text{TLS}} \otimes \hat{\rho}_{\text{sys},1}(t) \right] \\
&- \frac{1}{\hbar^2} \int_0^\infty \int_0^\infty d\tau d\omega J_{RC}(\omega) \coth \left( \frac{\beta \hbar \omega}{2} \right) \cos(\omega \tau) \left[ \hat{A}_1(t), \left[ \hat{A}_1(t - \tau), \hat{\rho}_{\text{sys},1}(t) \right] \right] \\
&+ \frac{i}{\hbar} \int_0^\infty \int_0^\infty d\tau d\omega J_{RC}(\omega) \sin(\omega \tau) \left[ \hat{A}_1(t), \left\{ \hat{A}_1(t - \tau), \hat{\rho}_{\text{sys},1}(t) \right\} \right].
\end{aligned}
\]  

(3.49)

(3.50)

(3.51)

(3.52)

We notice that the counter term (3.50) still appears in the master equation. It can be written in terms of \( J_{RC}(\omega) \) by noticing that \( \lambda = \sum_k \frac{g_k^2}{\omega_k} = \int_0^\infty d\omega \frac{1}{\omega} \sum_k g_k^2 \delta(\omega - \omega_k) = \int_0^\infty d\omega J_{RC}(\omega) \frac{1}{\omega} \). Focusing on the double integral in Eq. (3.52), by using integration by parts and the continuum definition of the Ohmic spectral density \( J_{RC}(\omega) = \gamma \omega e^{-\omega/\Lambda} \), it can be
shown that
\[
\int_0^\infty \int_0^\infty d\tau d\omega J_{\text{RC}}(\omega) \sin(\omega \tau) \hat{A}_1(t - \tau) = \int_0^\infty d\omega \frac{J_{\text{RC}}(\omega)}{\omega} \hat{A}_1(t) + \int_0^\infty \int_0^\infty d\tau d\omega J_{\text{RC}}(\omega) \cos(\omega \tau) \frac{\partial}{\partial \tau} \hat{A}_1(t - \tau). \tag{3.53}
\]

Refer to Appendix D for a full derivation of Eq. (3.53). In the interaction picture, the evolution of combined system operators \( \hat{O}_1 \) is given by
\[
\frac{d}{dt} \hat{O}_1(t) = -\frac{i}{\hbar} \left[ \hat{O}_1(t), \hat{H}_{0,S} \right], \tag{3.54}
\]
and we have by the chain rule that
\[
\frac{\partial \hat{A}_1(t - \tau)}{\partial \tau} = \frac{\partial (t - \tau)}{\partial (t - \tau)} \frac{\partial \hat{A}_1(t - \tau)}{\partial (t - \tau)} = -\frac{\partial \hat{A}_1(t - \tau)}{\partial (t - \tau)}. \tag{3.55}
\]
Combining Eqs. (3.54) and (3.55) we obtain
\[
\frac{\partial \hat{A}_1(t - \tau)}{\partial \tau} = -\frac{\partial \hat{A}_1(t - \tau)}{\partial (t - \tau)} = \frac{i}{\hbar} \left[ \hat{A}_1(t - \tau), \hat{H}_{0,S} \right]. \tag{3.56}
\]
Thus by substituting Eqs. (3.53) and (3.56) into (3.52), we obtain
\[
\frac{d}{dt} \hat{A}_1(t) = \frac{i}{\hbar} \left[ \hat{A}_1(t), \left\{ \int_0^\infty \int_0^\infty d\tau d\omega J_{\text{RC}}(\omega) \sin(\omega \tau) \hat{A}_1(t - \tau), \hat{\rho}_{\text{sys},1}(t) \right\} \right] \tag{3.57}
\]
\[
= \frac{i}{\hbar} \left[ \hat{A}_1(t), \left\{ \int_0^\infty d\omega \frac{J_{\text{RC}}(\omega)}{\omega} \hat{A}_1(t) \right\} \right. \tag{3.58}
\]
\[
+ \frac{i}{\hbar} \int_0^\infty \int_0^\infty d\tau d\omega J_{\text{RC}}(\omega) \cos(\omega \tau) \frac{\partial}{\partial \tau} \left[ \hat{A}_1(t - \tau), \hat{H}_{0,S} \right], \hat{\rho}_{\text{sys},1}(t) \right\} \right]
\]
\[
= \frac{i}{\hbar} \left[ \hat{A}_1(t), \left\{ \int_0^\infty d\omega \frac{J_{\text{RC}}(\omega)}{\omega} \hat{A}_1(t), \hat{\rho}_{\text{sys},1}(t) \right\} \right] \tag{3.59}
\]
\[
- \frac{1}{\hbar^2} \int_0^\infty \int_0^\infty d\omega d\tau J_{\text{RC}}(\omega) \frac{\cos(\omega \tau)}{\omega} \left[ \hat{A}_1(t), \left\{ \hat{A}_1(t - \tau), \hat{H}_{0,S} \right\}, \hat{\rho}_{\text{sys},1}(t) \right\} \right]. \tag{3.60}
\]
Recall that \( \tilde{\lambda} = \int_0^\infty d\omega \frac{J_{\text{RC}}(\omega)}{\omega} \); with this along with some algebraic manipulation we
can simplify term (3.59) as follows,

\[ (3.59) = \frac{i}{\hbar} \left[ \hat{A}_1(t), \left\{ \int_0^\infty d\omega \frac{J_{RC}(\omega)}{\omega} \hat{A}_1(t), \hat{\rho}_{\text{sys},1}(t) \right\} \right] \]

\[ = \frac{i\lambda}{\hbar} \left[ \hat{A}_1(t), \left\{ \hat{A}_1(t), \hat{\rho}_{\text{sys},1}(t) \right\} \right] \]

\[ = - \frac{i\lambda}{\hbar} \left[ \hat{A}_1(t) \left( \hat{A}_1(t)\hat{\rho}_{\text{sys},1}(t) + \hat{\rho}_{\text{sys},1}(t)\hat{A}_1(t) \right) \right. \]

\[ - \left( \hat{A}_1(t)\hat{\rho}_{\text{sys},1}(t) + \hat{\rho}_{\text{sys},1}(t)\hat{A}_1(t) \right) \hat{A}_1(t) \]

\[ = \frac{i\lambda}{\hbar} \left[ \hat{A}_1(t) \hat{A}_1(t)\hat{\rho}_{\text{sys},1}(t) - \hat{\rho}_{\text{sys},1}(t)\hat{A}_1(t) \hat{A}_1(t) \right] \]

\[ = \frac{i\lambda}{\hbar} \left[ \hat{A}_1^2(t), \hat{\rho}_{\text{sys},1}(t) \right]. \]

With the substitution \( \hat{A}_1^2(t) \to \hat{I}_{\text{TLS}} \otimes \hat{A}_1^2(t) \) we see that the counter term (3.50) is cancelled out exactly by Eq. (3.65), and now the master equation has the form

\[ \frac{\partial \hat{\rho}_{\text{sys},1}(t)}{\partial t} = -\frac{i}{\hbar} \left[ \hat{T}_1(t) \otimes \hat{I}_{\text{RC}}, \hat{\rho}_{\text{sys},1}(t) \right] \]

\[ - \frac{1}{\hbar} \int_0^\infty \int_0^\infty d\tau d\omega J_{RC}(\omega) \coth \left( \frac{\beta \hbar \omega}{2} \right) \cos(\omega \tau) \left[ \hat{A}_1(t), \left[ \hat{A}_1(t-\tau), \hat{\rho}_{\text{sys},1}(t) \right] \right] \]

\[ - \frac{1}{\hbar^2} \int_0^\infty \int_0^\infty d\omega d\tau J_{RC}(\omega) \frac{\cos(\omega \tau)}{\omega} \left[ \hat{A}_1(t), \left\{ \left[ \hat{A}_1(t-\tau), \hat{H}_{0,S} \right], \hat{\rho}_{\text{sys},1}(t) \right\} \right]. \]

To make numerical implementation of the master equation easier, we would like to remove the explicit time-dependence from within the integral terms on lines (3.67) and (3.68), which we can accomplish by switching the master equation back to the Scrodinger picture. We start by using the product rule as follows

\[ \frac{\partial \hat{\rho}_{\text{sys},S}(t)}{\partial t} = \frac{\partial}{\partial t} \left( e^{-\frac{i}{\hbar} \hat{H}_{0,st} t} \hat{\rho}_{\text{sys},1}(t) e^{\frac{i}{\hbar} \hat{H}_{0,st} t} \right) \]

\[ = -\frac{i}{\hbar} \hat{H}_{0,S} \hat{\rho}_{\text{sys},S}(t) + \frac{i}{\hbar} \hat{\rho}_{\text{sys},S}(t) \hat{H}_{0,S} + e^{-\frac{i}{\hbar} \hat{H}_{0,st} t} \left( \frac{\partial \hat{\rho}_{\text{sys},1}(t)}{\partial t} \right) e^{\frac{i}{\hbar} \hat{H}_{0,st} t} \]

\[ = -\frac{i}{\hbar} \left[ \hat{H}_{0,S}, \hat{\rho}_{\text{sys},S}(t) \right] + e^{-\frac{i}{\hbar} \hat{H}_{0,st} t} \left( \frac{\partial \hat{\rho}_{\text{sys},1}(t)}{\partial t} \right) e^{\frac{i}{\hbar} \hat{H}_{0,st} t}. \]

To compute (**), we only need to consider the commutator terms on lines (3.66),
(3.67), and (3.68), which assume the following forms:

\[ e^{-\frac{i}{\hbar}H_{0,\text{st}} t} \left( \hat{T}_I(t) \otimes \hat{I}_{\text{RC}}, \hat{\rho}_{\text{sys},1}(t) \right) e^{\frac{i}{\hbar}H_{0,\text{st}} t} = \left[ \hat{T}_S(t) \otimes \hat{I}_{\text{RC}}, \hat{\rho}_{\text{sys},S}(t) \right], \]  

(3.72)

\[ e^{-\frac{i}{\hbar}H_{0,\text{st}} t} \left( \hat{A}_1(t), \left[ \hat{A}_1(t - \tau), \hat{\rho}_{\text{sys},1}(t) \right] \right) e^{\frac{i}{\hbar}H_{0,\text{st}} t} = \left[ \hat{A}_S, \left[ \hat{A}_1(-\tau), \hat{\rho}_{\text{sys},S}(t) \right] \right], \]  

(3.73)

\[ e^{-\frac{i}{\hbar}H_{0,\text{st}} t} \left( \hat{A}_1(t), \left\{ \left[ \hat{A}_1(t - \tau), \hat{H}_{0,S} \right], \hat{\rho}_{\text{sys},1}(t) \right\} \right) e^{\frac{i}{\hbar}H_{0,\text{st}} t} = \left[ \hat{A}_S, \left\{ \left[ \hat{A}_1(-\tau), \hat{H}_{0,S} \right], \hat{\rho}_{\text{sys},S}(t) \right\} \right]. \]  

(3.74)

Combining Eqs. (3.72), (3.73), and (3.74) with Eq. (3.71) we arrive at the master equation in the Schrödinger picture

\[
\frac{\partial \hat{\rho}_{\text{sys},S}(t)}{\partial t} = -\frac{i}{\hbar} \left[ \hat{H}_{0,S}, \hat{\rho}_{\text{sys},S}(t) \right] - \frac{i}{\hbar} \left[ \hat{T}_S(t) \otimes \hat{I}_{\text{RC}}, \hat{\rho}_{\text{sys},S}(t) \right]  \\
- \frac{1}{\hbar^2} \int_0^\infty \int_0^\infty d\tau d\omega J_{\text{RC}}(\omega) \cos(\omega \tau) \left[ \hat{A}_S, \left[ \hat{A}_1(-\tau), \hat{\rho}_{\text{sys},S}(t) \right] \right]  \\
- \frac{1}{\hbar^2} \int_0^\infty \int_0^\infty d\omega d\tau J_{\text{RC}}(\omega) \frac{\cos(\omega \tau)}{\omega} \left[ \hat{A}_S, \left\{ \left[ \hat{A}_1(-\tau), \hat{H}_{0,S} \right], \hat{\rho}_{\text{sys},S}(t) \right\} \right].
\]  

(3.75)

We will now make the replacement \( \hat{A}_{S/1}(\bullet) \rightarrow \hat{I}_{\text{TLS}} \otimes \hat{A}_{S/1}(\bullet) \) to obtain the master equation for the case of a tuned TLS,

\[
\frac{\partial \hat{\rho}_{\text{sys},S}(t)}{\partial t} = -\frac{i}{\hbar} \left[ \hat{H}_{0,S}, \hat{\rho}_{\text{sys},S}(t) \right] - \frac{i}{\hbar} \left[ \hat{T}_S(t) \otimes \hat{I}_{\text{RC}}, \hat{\rho}_{\text{sys},S}(t) \right]  \\
- \frac{1}{\hbar^2} \left[ \hat{I}_{\text{TLS}} \otimes \hat{A}_S, [\hat{\chi}, \hat{\rho}_{\text{sys},S}(t)] \right] + \frac{1}{\hbar^2} \left[ \hat{I}_{\text{TLS}} \otimes \hat{A}_S, \left\{ \hat{\chi}, \hat{\rho}_{\text{sys},S}(t) \right\} \right],
\]  

(3.78)

where we have defined the operators,

\[
\hat{\chi} = \int_0^\infty \int_0^\infty d\tau d\omega J_{\text{RC}}(\omega) \cos(\omega \tau) \left( \frac{\beta \hbar \omega}{2} \right) \hat{I}_{\text{TLS}} \otimes \hat{A}_1(-\tau),
\]  

(3.79)

\[
\hat{\xi} = \int_0^\infty \int_0^\infty d\tau d\omega J_{\text{RC}}(\omega) \frac{\cos(\omega \tau)}{\omega} \left[ \hat{H}_{0,S}, \hat{I}_{\text{TLS}} \otimes \hat{A}_1(-\tau) \right],
\]  

(3.80)

and where \( \hat{A}_1(-\tau) = e^{-i\hat{H}_{0,\text{st}}/\hbar} \hat{A}_S e^{i\hat{H}_{0,\text{st}}/\hbar} \) is the interaction picture representation of \( \hat{A}_S \).

The multiplication by complicated matrix exponentials in the definition of \( \hat{A}_1(-\tau) \) makes it difficult to simplify analytically. For easier numerical implementation we can simplify the operators \( \hat{\chi} \) and \( \hat{\xi} \) by considering the orthonormal eigenbasis \( \{ |\varphi_n\rangle \}_{n \in \mathbb{N}} \)
of $\hat{H}_{0,S}$, so that $\hat{H}_{0,S} |\varphi_n\rangle = \varphi_n |\varphi_n\rangle$ for all $n \in \mathbb{N}$. In this basis we can express $\hat{H}_{0,S}$ and $\hat{I}_{\text{TLS}} \otimes \hat{A}_S$ as

$$\hat{H}_{0,S} = \sum_n \varphi_n |\varphi_n\rangle \langle \varphi_n|,$$  
(3.81)

$$\hat{I}_{\text{TLS}} \otimes \hat{A}_S = \sum_{jk} \langle \varphi_j| \hat{I}_{\text{TLS}} \otimes \hat{A}_S |\varphi_k\rangle |\varphi_j\rangle \langle \varphi_k| = \sum_{jk} A_{j,k} |\varphi_j\rangle \langle \varphi_k|.$$  
(3.82)

We note that by the spectral theorem the exponential of $\hat{H}_{0,S}$ is given by

$$e^{i\hat{H}_{0,S}t/\hbar} = \sum_n e^{i\varphi_n t/\hbar} |\varphi_n\rangle \langle \varphi_n|,$$  
(3.83)

so that in the interaction picture $\hat{I}_{\text{TLS}} \otimes \hat{A}_S$ becomes

$$\hat{I}_{\text{TLS}} \otimes \hat{A}_I(t) = e^{i\hat{H}_{0,S}t/\hbar} \left( \hat{I}_{\text{TLS}} \otimes \hat{A}_S \right) e^{-i\hat{H}_{0,S}t/\hbar}$$

$$= \sum_n e^{i\varphi_n t/\hbar} |\varphi_n\rangle \left( \sum_{jk} A_{j,k} |\varphi_j\rangle \langle \varphi_k| \right) \sum_m e^{-i\varphi_m t/\hbar} |\varphi_m\rangle \langle \varphi_m|$$

$$= \sum_{jk} A_{j,k} e^{i(\varphi_j - \varphi_k)t/\hbar} |\varphi_j\rangle \langle \varphi_k|.$$  
(3.84)

By defining $\xi_{jk} = \varphi_j - \varphi_k$, we have

$$\hat{I}_{\text{TLS}} \otimes \hat{A}_I(t) = \sum_{jk} A_{j,k} e^{i\xi_{jk} t/\hbar} |\varphi_j\rangle \langle \varphi_k|.$$  
(3.84)

Using Eqs. (3.79) and (3.84), we write the operator $\hat{\chi}$ as

$$\hat{\chi} = \int_0^\infty d\tau d\omega J_{\text{RC}}(\omega) \cos(\omega \tau) \coth \left( \frac{\beta \hbar \omega}{2} \right) \left( \sum_{jk} A_{j,k} e^{-i\xi_{jk} \tau/\hbar} |\varphi_j\rangle \langle \varphi_k| \right)$$

$$= \frac{1}{2} \sum_{jk} A_{j,k} |\varphi_j\rangle \langle \varphi_k| \int_0^\infty d\omega J_{\text{RC}}(\omega) \coth \left( \frac{\beta \hbar \omega}{2} \right) \int_0^\infty d\tau \left( e^{i(\omega - \xi_{jk}/\hbar)\tau} + e^{-i(\omega + \xi_{jk}/\hbar)\tau} \right).$$

Next, we employ the following result from Ref. [35]

$$\int_0^\infty e^{ikx} dk = \pi \delta(x) + i\sigma(x),$$  
(3.85)
where \( \sigma(x) = \lim_{\eta \to 0^+} \frac{x}{\pi^2 \eta^2} \), and \( \pi \delta(x) = \lim_{\eta \to 0^+} \frac{\eta}{\pi^2 \eta^2} \). With the above result the integral for \( \hat{\chi} \) is simplified to

\[
\hat{\chi} = \frac{1}{2} \sum_{jk} A_{j,k} |\varphi_j\rangle \langle \varphi_k| \int_0^\infty d\omega J_{RC}(\omega) \coth\left( \frac{\beta \hbar \omega}{2} \right) \left( \int_0^\infty d\tau e^{i(\omega - \xi_{jk}/\hbar)\tau} + \int_0^\infty d\tau e^{-i(\omega + \xi_{jk}/\hbar)\tau} \right)
\]

\[
= \frac{1}{2} \sum_{jk} A_{j,k} |\varphi_j\rangle \langle \varphi_k| \int_0^\infty d\omega J_{RC}(\omega) \coth\left( \frac{\beta \hbar \omega}{2} \right) \left[ \pi \delta(\omega - \xi_{jk}/\hbar) + i\sigma(\omega - \xi_{jk}/\hbar) + \pi \delta(\omega + \xi_{jk}/\hbar) - i\sigma(\omega + \xi_{jk}/\hbar) \right].
\]

At this point, we ignore the imaginary terms in \( \hat{\chi} \) which correspond to Lamb shifts \([6, 10]\), justified by the assumption that they are negligible in comparison to \( \sqrt{\varepsilon^2 + \hbar^2 \Delta^2} \). Hence, \( \hat{\chi} \) can be approximated by

\[
\hat{\chi} \approx \frac{\pi}{2} \sum_{jk} A_{j,k} |\varphi_j\rangle \langle \varphi_k| \int_0^\infty d\omega J_{RC}(\omega) \coth\left( \frac{\beta \hbar \omega}{2} \right) \left[ \delta(\omega - \xi_{jk}/\hbar) + \delta(\omega + \xi_{jk}/\hbar) \right]
\]

\[
= \frac{\pi}{2} \sum_{jk} J_{RC}(\xi_{jk}/\hbar) \coth\left( \frac{\beta \xi_{jk}}{2} \right) A_{j,k} |\varphi_j\rangle \langle \varphi_k|.
\]
We can similarly simplify the expression for the operator $\hat{\Xi}$,

$$
\hat{\Xi} = \int_0^\infty \int_0^\infty d\tau d\omega \frac{J_{RC}(\omega) \cos(\omega \tau)}{\omega} \left[ \hat{H}_{0,S} \sum_{jk} A_{j,k} e^{-i\xi_{jk}/\hbar} |\varphi_j\rangle \langle \varphi_k| \right]
$$

$$
= \int_0^\infty \int_0^\infty d\tau d\omega \frac{J_{RC}(\omega) \cos(\omega \tau)}{\omega} \sum_{jk} A_{j,k} e^{-i\xi_{jk}/\hbar} \left( \hat{H}_{0,S} |\varphi_j\rangle \langle \varphi_k| - |\varphi_j\rangle \langle \varphi_k| \hat{H}_{0,S} \right)
$$

$$
= \int_0^\infty \int_0^\infty d\tau d\omega \frac{J_{RC}(\omega) \cos(\omega \tau)}{\omega} \sum_{jk} A_{j,k} e^{-i\xi_{jk}/\hbar} |\varphi_j\rangle \langle \varphi_k|
$$

$$
= \frac{1}{2} \sum_{jk} A_{j,k} \xi_{jk} |\varphi_j\rangle \langle \varphi_k| \int_0^\infty d\omega J_{RC}(\omega) \left( \int_0^\infty d\tau e^{i(\omega-\xi_{jk}/\hbar)\tau} + \int_0^\infty d\tau e^{-i(\omega+\xi_{jk}/\hbar)\tau} \right)
$$

$$
\approx \frac{\pi}{2} \sum_{jk} A_{j,k} \xi_{jk} |\varphi_j\rangle \langle \varphi_k| \int_0^\infty d\omega J_{RC}(\omega) \omega \left[ \delta(\omega - \xi_{jk}/\hbar) + \delta(\omega + \xi_{jk}/\hbar) \right]
$$

$$
= \frac{\pi}{2} \sum_{jk} A_{j,k} \xi_{jk} |\varphi_j\rangle \langle \varphi_k| J_{RC}(\xi_{jk}/\hbar) \xi_{jk}/\hbar
$$

$$
= \frac{\pi\hbar}{2} \sum_{jk} J_{RC}(\xi_{jk}/\hbar) A_{j,k} |\varphi_j\rangle \langle \varphi_k|.
$$

And hence, we find that the operators $\hat{\chi}$ and $\hat{\Xi}$ can be approximated by

$$
\hat{\chi} \approx \frac{\pi}{2} \sum_{jk} J_{RC}(\xi_{jk}/\hbar) \coth \left( \frac{\beta \xi_{jk}}{2} \right) A_{j,k} |\varphi_j\rangle \langle \varphi_k| , \quad (3.86)
$$

$$
\hat{\Xi} \approx \frac{\pi\hbar}{2} \sum_{jk} J_{RC}(\xi_{jk}/\hbar) A_{j,k} |\varphi_j\rangle \langle \varphi_k|. \quad (3.87)
$$

Hence, we have shown that the reaction coordinate master equation from Ref. [10] applies also in the case of a time-dependent TLS. Furthermore, we note that the RC master equation in Eq. (3.78) is not of Lindblad form, as defined in Eq. (2.29). We expect the RC master equation to be non-Markovian, so this is not surprising, but it also means that the evolution of the density operator is not guaranteed to preserve positivity.
Chapter 4

Numerical results in the superconducting qubit regime

The reaction coordinate master equation, Eq. (3.78), is computationally demanding when compared to standard Markovian approaches. The justification for the additional computation cost is the expectation that in certain regimes the Markovian approach will fail to produce meaningful (or even physical) results, whereas the reaction coordinate master equation will not. This chapter begins by testing the positivity of the reaction coordinate master equation numerically. We then introduce a particular Markovian master equation from Ref. [36] which is compared to the reaction coordinate master equation derived in the previous chapter. We compare the differences in modelled dynamics in superconducting qubit regime, and then analyze the decoherence rates predicted by the two dynamical equations in the Markovian regime. We end the chapter by investigating the use of time-dependent bias for improving qubit coherence.

4.1 Positivity of solutions

We expect the reaction coordinate master equation from Eq. (3.78) to be able to model spin-boson dynamics in more detail than simpler dynamical equations with heavier approximations, however several approximations were made in the derivation and hence there may be some parameter combinations which produce unphysical results.

Analytically determining the parameter combinations which preserve complete positivity or just positivity for the master equation is a difficult problem, however it is simple to check for positivity violations numerically. One way to accomplish this is by checking whether any of the diagonal terms of the density matrix of the TLS-RC system are either greater than one or less than zero. In other words, we check whether
the system contains probabilities greater than one or less than zero.

Our primary interest in this work is the modelling of qubits in the superconducting regime, and hence we are only concerned with checking the range of validity of the reaction coordinate master equation within parameter ranges corresponding to superconducting qubit systems. Typical superconducting qubit frequencies are in the range of 5-20 GHz with an environment temperature of about 20 mK [37]. In Ref. [30] reaction coordinate spin-boson parameters were determined for a superconducting qubit system based on two physically realized flux qubits; the parameters are summarized in Table 4.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Qubit 1</th>
<th>Qubit 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta/2\pi$</td>
<td>3.4 GHz</td>
<td>0.66 GHz</td>
</tr>
<tr>
<td>$\varepsilon/2\pi$</td>
<td>4.59 GHz</td>
<td>0</td>
</tr>
<tr>
<td>$\Omega/2\pi$</td>
<td>2.01 GHz</td>
<td>0.6138 GHz</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>0.0078</td>
<td>0.014</td>
</tr>
<tr>
<td>$\lambda/2\pi$</td>
<td>0.0272 GHz</td>
<td>0.04158 GHz</td>
</tr>
<tr>
<td>$T$</td>
<td>25 mK</td>
<td>30 mK</td>
</tr>
</tbody>
</table>

Table 4.1: Physically realized flux qubit parameters. Qubit 1 is described in Ref. [38], whereas details of Qubit 2 can be found in Ref. [39].

Numerical checks for positivity violations using parameter combinations of $\Delta/2\pi$ and $\varepsilon/2\pi$ with ranges 1-8 GHz, $\lambda/2\pi$ with 0.01-0.05 GHz, and $\Omega/2\pi$ with 0.5-2 GHz, at both 10 mK and 30 mK temperatures yielded no positivity violations. This suggests that for typical superconducting qubit parameter ranges the reaction coordinate master equation does not violate positivity, although this is by no means an exhaustive check of positivity. In addition, complete positivity may still be violated even if positivity is not.

By widening the parameter ranges, positivity violations can be found. Fixing the qubit frequency, temperature, and coupling strength $\gamma$ and testing with larger values of $\lambda$ and $\Omega$, we find positivity violations as $\Omega$ approaches the order of 10 GHz, as seen in Fig. 4.1.

However, if the condition for positivity violation is loosened such that we demand that the density matrix diagonals are strictly less than 1, but only need to be greater than $-0.01$ rather than 0, then we find that the positivity violations disappear. This could mean that for the parameter ranges considered in Fig. 4.1 the positivity violations are not severe, or that they are actually errors due to numerical accuracy limits. By considering even broader parameter ranges severe violations can be found, although it is not certain whether the parameters at these ranges correspond to anything physically meaningful for our purposes.
Figure 4.1: Positivity violations of the reaction coordinate master equation for combinations of $\lambda/2\pi$ and $\Omega/2\pi$ ranging from $10^{-3}$ GHz to $10^3$ GHz. Fixed parameters are $\Delta/2\pi = \varepsilon/2\pi = 5$ GHz, $\gamma = 0.01$, and $T = 30$ mK.

It would be safest to perform a quick check of positivity when choosing to work with a new parameter range.

### 4.2 Markovian master equation in the spin-boson model

We refer to the Markovian master equation from Ref. [36], given in the Schrödinger picture by the coupled differential equations,

\[ \frac{d\rho_{gg}}{dt} = - (\Gamma_{ge} + \Gamma_{eg}) \rho_{gg} + \text{Re} \left\{ \hat{\Gamma}_0 \rho_{ge} \right\} + \Gamma_{eg}, \]  

\[ \frac{d\rho_{ge}}{dt} = i\omega_{01}\rho_{ge} - (\hat{\Gamma}_+ + \hat{\Gamma}_-)\rho_{gg} - \left( \frac{\Gamma_{eg}}{2} + \frac{\Gamma_{ge}}{2} + \Gamma_\varphi \right) \rho_{ge} + (\Gamma_\alpha + \Gamma_\beta)\rho_{eg} + \hat{\Gamma}_+, \]

where $\omega_{01} = (E_e - E_g)/\hbar$ and $\rho_{ab} = \langle a|\hat{\rho}_S|b \rangle$ for $a, b \in \{e, g\}$. Furthermore, $|e\rangle, E_e$ and $|g\rangle, E_g$ are the excited state (energy) and ground state (energy) of the TLS, respectively.

For the spin-boson interaction Hamiltonian, $\hat{H}_I = \hat{\sigma}_z \otimes \hat{X}$, where we define the
bath force operator to be $\hat{X} = \sum_k f_k (\hat{c}_k^\dagger + \hat{c}_k)$, the rates are given by

$$
\Gamma_{ge} = \frac{|\langle e|\hat{\sigma}_z|g\rangle|^2}{\hbar^2} S_X(-\omega_{01}), \\
\Gamma_{eg} = \frac{|\langle e|\hat{\sigma}_z|g\rangle|^2}{\hbar^2} S_X(\omega_{01}), \\
\tilde{\Gamma}_0 = \frac{\langle e|\hat{\sigma}_z|g\rangle (\langle g|\hat{\sigma}_z|g\rangle - \langle e|\hat{\sigma}_z|e\rangle)}{\hbar^2} S_X(0), \\
\tilde{\Gamma}_{\pm} = \frac{\langle g|\hat{\sigma}_z|e\rangle (\langle e|\hat{\sigma}_z|e\rangle - \langle g|\hat{\sigma}_z|g\rangle)}{2\hbar^2} S_X(\pm\omega_{01}), \\
\Gamma_{\varphi} = \left( \frac{\langle e|\hat{\sigma}_z|e\rangle^2}{2\hbar^2} + \frac{\langle g|\hat{\sigma}_z|g\rangle^2}{\hbar^2} - \frac{\langle g|\hat{\sigma}_z|g\rangle \langle e|\hat{\sigma}_z|e\rangle}{\hbar^2} \right) S_X(0), \\
\Gamma_{\alpha} = \frac{\langle g|\hat{\sigma}_z|e\rangle^2}{2\hbar^2} S_X(\omega_{01}), \\
\Gamma_{\beta} = \frac{\langle g|\hat{\sigma}_z|e\rangle^2}{2\hbar^2} S_X(-\omega_{01}).
$$

In order to compare the dynamics of the Markovian equation, Eqs. (4.1), (4.2), to the non-Markovian master equation (3.78), we must relate the power spectral density $S_X(\omega)$ to the bath spectral density $J_{SB}(\omega)$. This can be done using relations found in Refs. [40–42]:

$$
\begin{align*}
\bar{S}_X(\omega) &= \frac{1}{2} \int_{-\infty}^{\infty} dt e^{i\omega t} \left\langle \left\{ \hat{X}(0), \hat{X}(-t) \right\} \right\rangle = \hbar J_{SB}(\omega) \coth \left( \frac{\beta \hbar \omega}{2} \right), \\
\bar{S}_X(\omega) &= \frac{1}{2} (S_X(\omega) + S_X(-\omega)), \\
\frac{S_X(\omega)}{S_X(-\omega)} &= e^{\beta \hbar \omega}.
\end{align*}
$$

Using the above, we get the following relationships between the bath spectral density and power spectrum,

$$
\begin{align*}
S_X(\omega) &= \frac{2\hbar}{1 + e^{-\beta \hbar \omega}} \coth \left( \frac{\beta \hbar \omega}{2} \right) J_{SB}(\omega), \\
S_X(-\omega) &= \frac{2\hbar}{1 + e^{\beta \hbar \omega}} \coth \left( \frac{\beta \hbar \omega}{2} \right) J_{SB}(\omega).
\end{align*}
$$

The zero frequency term, $S_X(0)$, requires some care due to the divergence of the hyperbolic cotangent function at the origin. This can be resolved by defining $S_X(0)$ as a limit,

$$
S_X(0) = \lim_{\omega \to 0^+} S_X(\omega) = \frac{8\gamma \lambda^2}{\beta \Omega^2}.
$$
4.3. COMPARISON TO MARKOVIAN DYNAMICS

The eigenstates of the TLS ($|e\rangle$, $|g\rangle$) can be related to the eigenstates of the $\hat{\sigma}_z$ operator ($|1\rangle$, $|2\rangle$) by the equations

$$|1\rangle = \cos \left( \frac{\theta}{2} \right) |e\rangle - \sin \left( \frac{\theta}{2} \right) |g\rangle,$$

$$|2\rangle = \sin \left( \frac{\theta}{2} \right) |e\rangle + \cos \left( \frac{\theta}{2} \right) |g\rangle,$$

where

$$\cos \left( \frac{\theta}{2} \right) = \sqrt{\frac{\sqrt{\varepsilon^2 + \Delta^2} + \varepsilon}{2\sqrt{\varepsilon^2 + \Delta^2}}},$$

$$\sin \left( \frac{\theta}{2} \right) = \sqrt{\frac{\sqrt{\varepsilon^2 + \Delta^2} - \varepsilon}{2\sqrt{\varepsilon^2 + \Delta^2}}}.$$

A derivation of these equations can be found in Appendix B.

We employ the following notation for the density operator and its matrix representation

| Definition | 
|-------------------------------|---------------------|
| $\hat{\rho}^\text{rc}$ | TLS density operator in the reaction coordinate model, $\text{Tr}_{\text{RC}}(\hat{\rho}_{\text{sys},S})$ |
| $\hat{\rho}^\text{M}$ | TLS density operator in the Markovian model |
| $\rho^x_{ee}$ | $\langle e | \hat{\rho}^x | e \rangle$ |
| $\rho^x_{11}$ | $\langle 1 | \hat{\rho}^x | 1 \rangle$ |

where $x$ can be either $\text{rc}$ or $\text{M}$. All density operators are in the Schrödinger picture in the rest of this thesis, so we omit the subscript $S$.

4.3 Comparison of Markovian and reaction coordinate dynamics

In this section we compare the modelled dynamics of superconducting qubits using the parameter values of real flux qubits, listed in Table 4.1.

For the numerical implementation of the RC master equation, we need to choose finite truncation of the RC Hilbert space dimension, $n$. In Ref. [30] a truncation of $n = 6$ was found to be sufficient in modelling superconducting qubits; a quick comparison of density matrices produced with a truncation of $n = 6$ versus $n = 12$ results in less than 1% difference, confirming that it is sufficient to restrict the reaction coordinate to 6 modes.
We first consider Qubit 2, which has a stronger coupling between the qubit and
the environment, with a dimensionless coupling factor of \( \alpha \approx 1.28 \times 10^{-4} \), and hence
displays more dramatic short time behaviour. Setting the initial state of the TLS to be
its excited state \( |e\rangle \), we can compare the reaction coordinate and Markovian dynamics
of how the qubit thermalizes to its equilibrium state with the bath, shown in Fig. 4.2.
We see that over long time scales the dynamics are quite similar, but from the start
of the simulation until about 25 ns the Markovian master equation fails to model
the system–bath correlations, which have a significant effect on the system behaviour.
The reaction coordinate master equation shows the excited state population increasing
near 8 ns, meaning that the TLS is getting energy back from the bosonic bath for
a brief moment before decaying to the equilibrium value. The equilibrium values also
differ slightly, being \( \rho_{ee}^R(t \to \infty) \approx 0.2587 \) in the reaction coordinate model, and
\( \rho_{ee}^M(t \to \infty) \approx 0.2581 \) in the Markovian model. The off-diagonal terms \( \rho_{eg/ge} \) are
negligible in both models, being smaller than \( 10^{-8} \) in the reaction coordinate model
and exactly zero in the Markovian model.

![Figure 4.2: Evolution of the excited state population, \( \rho_{ee} \), with the excited state
\( \hat{\rho}(0) = |e\rangle \langle e| \) as the initial state of the TLS. Solid line corresponds to results from the
reaction coordinate master equation, whereas the dashed line corresponds to results
from the Markovian master equation. System parameters are set to match Qubit 2 in
Table 4.1.](image)

This means that, in this case, the dynamics of the TLS can be described as a
convex combination of the excited state and the ground state

\[
\hat{\rho}(t) = \rho_{ee}(t) |e\rangle\langle e| + [1 - \rho_{ee}(t)] |g\rangle\langle g|.
\] (4.13)

This is identical to the toy example from Section 2.1 of the machine which fires electrons in spin up and spin down states with probabilities \(p\) and \((1 - p)\), except we now have a time-varying probability \(\rho_{ee}(t)\). Thus, we also have that the purity of the state of the TLS is given by

\[
\zeta(t) = \text{Tr}[\hat{\rho}(t)^2] = \rho_{ee}(t)^2 + [1 - \rho_{ee}(t)]^2.
\] (4.14)

Comparisons of the reaction coordinate and Markovian purities can be seen in Fig. 4.3. Since the initial state is the pure state \(|e\rangle\), the purity for both the reaction coordinate and the Markovian model begins at exactly \(\zeta(0) = 1\). The maximally mixed state is attained when \(\rho_{ee}(t) = 1/2\), which occurs at different times for the two models because of the fast initial decay in the reaction coordinate model. Interestingly, the local maximum of \(\rho_{ee}^\text{rc}(t)\) almost reaches the maximally mixed state exactly when the Markovian model reaches it, at about \(t = 8\) ns.

![Figure 4.3](image_url)

Figure 4.3: Evolution of the purity, \(\zeta = \text{Tr}(\hat{\rho}^2)\), with the excited state \(\hat{\rho}(0) = |e\rangle\langle e|\) as the initial state of the TLS. Solid line corresponds to results from the reaction coordinate master equation, whereas the dashed line corresponds to results from the Markovian master equation. System parameters are set to match Qubit 2 in Table 4.1.
Next we consider the same parameters but with the TLS initial state \( \hat{\rho}(0) = |1\rangle\langle 1| \), the eigenstate of the \( \hat{\sigma}_z \) operator corresponding to the +1 eigenvalue. This state can be written in terms of the TLS eigenstates as

\[
|1\rangle\langle 1| = \cos^2\left(\frac{\theta}{2}\right) |e\rangle\langle e| + \sin^2\left(\frac{\theta}{2}\right) |g\rangle\langle g| - \sin\left(\frac{\theta}{2}\right) \cos\left(\frac{\theta}{2}\right) (|e\rangle\langle g| + |g\rangle\langle e|),
\]

where the cosine and sine terms are as defined in Eqs.(4.11) and (4.12). We note that Qubit 2 has a bias term of zero (\( \varepsilon = 0 \)), which means that \( \cos^2(\theta/2) = \sin^2(\theta/2) = 1/2 \), and hence for Qubit 2 parameters, Eq. (4.15) reduces to the simple form

\[
|1\rangle\langle 1| = \frac{1}{2} \hat{I}_{\text{TLS}} - \frac{1}{2} (|e\rangle\langle g| + |g\rangle\langle e|).
\]

For this initial condition we get qualitatively the same dynamics for the diagonal terms as in the case of the TLS excited state being the initial state, except scaled by a half. The interesting parts are the off-diagonals, which now exhibit notable activity. In both the reaction coordinate and the Markovian settings the plots of \( \rho_{eg} \) versus time look like exponentially decaying sinusoids. However, the period and decay rate differs between the two models, as can be seen in Fig. 4.4.

![Figure 4.4: Evolution of the off-diagonal component, \( \rho_{eg} \), with initial state \( \hat{\rho}(0) = |1\rangle\langle 1| \). Top: reaction coordinate master equation dynamics, reaching equilibrium in about 30 ns. Bottom: Markovian master equation dynamics, reaching equilibrium in about 80 ns.](image-url)
4.3. COMPARISON TO MARKOVIAN DYNAMICS

The decay in the reaction coordinate model is considerably faster, indicating that the Markovian models is ill-suited for capturing decoherence effects. This is investigated further in the next section.

The differences in the dynamics thus far seem to indicate that the reaction coordinate model is able to model memory effects between the system and the bath, and is hence non-Markovian. To assess this more quantitatively we use the distinguishability criterion introduced in section 2.4, and compare the evolution of the trace distance between the reaction coordinate and Markovian models for the two initial states, \( \hat{\rho}_1(0) = |e\rangle\langle e| \) and \( \hat{\rho}_2(0) = |1\rangle\langle 1| \). Recall that the distinguishability, \( D \), of two states, \( \hat{\rho}_1 \) and \( \hat{\rho}_2 \), is given by Eq. (2.26), which can further be simplified thanks to the hermiticity of the density operator into the form

\[
D(\hat{\rho}_1, \hat{\rho}_2) = \frac{1}{2}\|\hat{\rho}_1 - \hat{\rho}_2\|_{\text{tr}} = \frac{1}{2} \sum_{\lambda} |\lambda|, \tag{4.17}
\]

where \( \lambda \) are eigenvalues of the difference operator \( \hat{\rho}_1 - \hat{\rho}_2 \).

Figure 4.5: Distinguishability of the states \( \hat{\rho}_1 \) and \( \hat{\rho}_2 \), where \( \hat{\rho}_1(0) = |e\rangle\langle e| \), \( \hat{\rho}_2(0) = |1\rangle\langle 1| \). The Markovian curve (dashed line) is monotonically decreasing, as expected, while the reaction coordinate model curve (solid line) displays an interval of substantial increase between 6 ns and 8 ns, indicating non-Markovianity.

In Fig. 4.5 we see the evolution of the distinguishability in time for both the reaction coordinate and Markovian models. As expected, the Markovian master equation
produces a monotonically decreasing function, as do all Markovian models. In contrast, the reaction coordinate master equation is clearly not monotonic, and has a significant region of non-monotonicity between 6 ns and 8 ns. This is a strong indication that the reaction coordinate master equation is able to model non-Markovian dynamics.

We now turn our attention to Qubit 1 from Table 4.1, which has a non-zero bias term and a weaker TLS-bath coupling of $\alpha = 2.87 \times 10^{-6}$, or about 45 times smaller than the coupling factor for Qubit 2. We expect a longer relaxation time due to the considerably weaker coupling to the environment, and in Fig. 4.6 we see that with the initial state set as the TLS excited state $|e\rangle$, the population $\rho_{ee}$ of the excited state remains very high even on time scales on the order of microseconds. The decay of the excited state is so slow that it appears linear for both the reaction coordinate and Markovian models at reasonably computable time scales. We do note however that at least for the first 10 microseconds, the Markovian model decays slower than the reaction coordinate model. The slow decay of Qubit 1 also means that it is not computationally reasonable to determine the relaxation time, even with the Markovian master equation which is considerably faster to compute than the reaction coordinate master equation. Inspecting the dynamics at shorter times shows that the reaction coordinate model does display oscillatory behaviour initially, which quickly dampens.

![Figures 4.6](image)

Figure 4.6: Decay of the excited population, $\rho_{ee}$, with the initial $\hat{\rho}(0) = |e\rangle\langle e|$. Parameters are those of Qubit 1 in Table 4.1. (a) Times up to 10 microseconds. (b) Times up to 20 nanoseconds.

The long life of the excited state in Qubit 1 also means that we can expect the state $\hat{\rho} = |1\rangle\langle 1|$ to decay very slowly, which is the case in the numerical simulations. Furthermore, the reaction coordinate and Markovian master equations produce very similar results for the evolution of the $\rho_{11}$ population, both modelling the decaying
oscillation of the qubit. The decay is slower in the Markovian model, and there is some disagreement in the period of oscillation. However, for short time-scales the two models agree to a high degree. Fig. 4.7 shows the evolution of the difference $\rho_{11}^c - \rho_{11}^M$.

Figure 4.7: Difference between the evolution of the $\rho_{11}$ population between the reaction coordinate and Markovian models.

4.4 Decay rates under decoherence

We recall from Section 2.3 that the relaxation time $T_1$ and the coherence time $T_2$ model the long time scale rates of decay of the TLS density matrix diagonal and off-diagonal terms, respectively. The physical limit for the coherence time is bounded by the relaxation time by $T_2 \leq 2T_1$, and the deviation from this limit can be quantified by the pure dephasing time, $T_\phi$, defined by the phenomenological relation,

$$\frac{1}{T_\phi} = \frac{1}{T_2} - \frac{1}{2T_1}. \quad (4.18)$$

To compute $T_1$ and $T_2$ we use a simple exponential fit. For the relaxation time the exponential fit can be applied directly to $\rho_{ee}$, although if there are non-Markovian effects at short time-scales it may be better to omit times in the interval $(0, \tau_b)$ from the fitting process, where $\tau_b$ is the approximate duration of the TLS-bath correlations. For the coherence time we apply the exponential fit to the positive peaks of $\rho_{eg}$, which
is typically a damped oscillating function. That is, we find the exponential envelope. Applying the exponential fits for the case of Qubit 2 from Table 4.1 with initial state $\hat{\rho}(0) = |1\rangle\langle 1|$, the naive fit for $\rho_{ee}^c$, where we apply the exponential fit for the whole curve, gives a $T_1$ value of about 3.6 ns, compared to the Markovian value of 7.6 ns. However, by omitting the points corresponding to times in the range $(0, 30)$ ns from $\rho_{ee}^c$, the fit then produces a $T_1$ value of 7.4 ns, which is very close to the Markovian value. Since the relaxation times are meant to characterize the long time-scale behaviour, the time it takes for the system to reach equilibrium, we use this corrected value to represent the reaction coordinate relaxation time. The coherence times are more straightforward, and we get results summarized in Table 4.2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>RC</th>
<th>Markovian</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_1$</td>
<td>7.4 ns</td>
<td>7.6 ns</td>
</tr>
<tr>
<td>$T_2$</td>
<td>3.6 ns</td>
<td>15.1 ns</td>
</tr>
<tr>
<td>$T_\phi$</td>
<td>4.8 ns</td>
<td>2300 ns</td>
</tr>
</tbody>
</table>

Table 4.2: Modelled relaxation times for Qubit 2.

The reaction coordinate method produces a dephasing time of $T_\phi \approx 5$ ns, which agrees with the modelled results in Ref. [39], and differs from the measured dephasing time of $T_\phi \approx 10$ ns by a factor of 2. In contrast, the Markovian model’s overestimation of the coherence time produces a grossly incorrect dephasing time on the order of 2 microseconds. It is of interest to note that the Markovian model does not violate the inequality $T_2 \leq 2T_1$, although it is very close to the equality case.

By increasing the bias $\varepsilon$ we can also increase the relaxation and coherence times. Following ideas from Refs. [43,44], we consider a time-dependent control field for the bias term of the form

$$\varepsilon(t) = \varepsilon_0 + A \cos(\omega_c t + \phi),$$

(4.19)

where $\varepsilon_0$ is the unperturbed bias, and the amplitude $A$, angular frequency $\omega_c$, and phase shift $\phi$ are free parameters of the plane wave control field. The idea behind the external control field is to be able to adjust the qubit bias term through an external control, hence adjusting the decoherence rates and possibly other properties with the appropriate choice of control field. We continue with modified Qubit 2 parameters where the bias $\varepsilon$ is adjusted, and we analyse how the evolution of the qubit is affected. We compare the time-varying bias given by Eq. (4.19) with baseline $\varepsilon_0/2\pi = 0.1$ GHz to two constant biases set to $\varepsilon/2\pi = 0.1$ GHz and $\varepsilon/2\pi = 0.2$ GHz. Through trial and error, with an initial state of $\hat{\rho}(0) = |e\rangle\langle e|$, we find that the parameters $A/2\pi = -0.2$ GHz, $\omega_c/2\pi = 0.167$ GHz, and $\phi = 0$ produce promising results, as shown in
4.4. DECAY RATES UNDER DECOHERENCE

Figure 4.8: Comparison of excited state decay profiles for the modified Qubit 2 with constant bias terms $\epsilon/2\pi = 0.1$ GHz and $\epsilon/2\pi = 0.2$ GHz, as well as a time-varying bias term $\epsilon(t)/2\pi = 0.1 - 0.1\cos(2\pi t/6)$ GHz. (a) Excited state decay profiles. (b) Time-varying bias through external control field.

The decay of the excited state with the time-varying bias lies in-between the decay profiles for the $\epsilon/2\pi = 0.1$ GHz and $\epsilon/2\pi = 0.2$ GHz constant biases. The controlled bias surpasses the performance of the lower constant bias with the same average amplitude of 0.1 GHz. The higher constant bias decay profile acts almost as an upper bound, excepting the late time intersections due to the oscillations from the control field.

Using the initial state $\hat{\rho}(0) = |1\rangle\langle 1|$ shows that comparable improvements are also seen for the coherence times with the time-varying bias. This means that a control field that is weaker than the tunnelling rate of the qubit can still improve the coherence time of the qubit.

Increasing the amplitude and frequency of the control field can produce a trapping effect where the excited state is prevented from decaying. The control field parameters from Ref. [44] which produce this trapping result are given by $A = 218.196\Delta$, $\omega_c = 89.996\Delta$, and $\phi = -1.119$ rad, where $\Delta/2\pi = 0.66$ Ghz. In our numerical implementation these parameters produce numerical instability after 10 ns, resulting in severe positivity violations. Regardless, for the first 6 ns this control field does seem to exhibit trapping for the qubit excited state, as seen in Fig. 4.9.

It may be possible to avoid the positivity violations by increasing the dimension of the RC Hilbert space, however this increases computational cost which is already very high for high frequencies. Furthermore, doubling the dimension of the RC Hilbert
Figure 4.9: Decay profile for Qubit 2 with a time-varying bias term $\varepsilon(t)/2\pi = 144 \cos[2\pi(59.4)t - 1.119]$ GHz. (a) Time range of physical values. (b) Full time range, with severe positivity violations.

These results show indications that further investigation into the choice of control field, as well as the possibility of allowing for a controlled tunnelling rate $\Delta$, can improve qubit coherence times.
Chapter 5

Discussion

The feasibility of quantum computers hinges on the ability to improve qubit coherence times. In 2013, a qubit coherence time of 39 minutes was achieved at room temperature, and a coherence time on the order of 3 hours at a temperature of 1.2 K [45], and work is ongoing. Driven qubit schemes have shown promise in being able to reduce decoherence using external control fields [43], making it important to have an accurate theoretical model for further developing these results.

In this thesis we have derived a reaction coordinate master equation for the spin-boson model which permits time-dependence in the two-level system. It was shown that this master equation is able to model non-Markovian behaviour between the system and environment, and predicts considerably different dynamics for short times when compared to a Markovian master equation. We also showed that within typical superconducting qubit parameter ranges, our master equation preserves positivity of the density operator. The derivation of the master equation assumes that the reaction coordinate representation has an Ohmic spectral density with an exponential cutoff. In order to relate this representation to the spin-boson model, we assumed an infinite cutoff for the frequencies, and arrived at a spectral density for the spin-boson system given in Eq. (2.42). A different choice of spectral density would also necessitate changing the classical equations of motion which relate the spectral densities between the two representations, and the RC–bath coupling strength $\gamma$ would need to be generalized to have a frequency dependence [12]. Thus, the reaction coordinate approach does not easily allow for changes in the spectral density.

In Section 4.2 we referred to a Markovian master equation from Ref. [36] and determined the relationship between its parameters and our reaction coordinate master equation parameters. Once we had found how these two master equations relate to each other, we proceeded in Sections 4.3 and 4.4 by using them to perform numerical modelling of the physically realized flux qubits, described in Table 4.1. Qubit 1
showed a very long relaxation time for both models, however the rates of decay were
noticeably different. For Qubit 2 we saw a short relaxation time, as well as TLS–bath
correlations for short times in the reaction coordinate model which were unsurpris-
ingly missing in the Markovian model. The relaxation times were comparable if the
early correlations are ignored in the RC model, but the coherence times were very
different regardless. In fact, the Markovian model predicted near equality for the
limiting case $T_2 \leq 2T_1$, and hence also predicted a very long dephasing time. The RC
model, in contrast, found values which agreed with previous work in Ref. [30].

We ended Section 4.4 by considering a time-dependent bias in the TLS. We found
that even at a lower amplitude and frequency range on the same order as Qubit
2, we were able to find parameters for the plane wave control field which qualita-
tively improved relaxation and decoherence times, although marginally. Attempting
to implement the optimal trapping control field from Ref. [44] for Qubit 2 resulted in
numerical instability, making the results unreliable. Still, there were indications that
for a control field with very high amplitude and frequency, it is possible to trap the
qubit in its excited state for some time. It would be worth investigating how much
decoherence can be controlled with more exotic control fields.
Bibliography


Appendix A

Computation of spin-boson spectral density using classical equations of motion

We will follow methods outlined in Refs. [10, 12, 27, 46]. To start, the spin-boson Hamiltonian in Eq. (2.30) can be transformed into position/momentum form using the definitions,

\[ \hat{x}_k = \sqrt{\frac{1}{2\nu_k}} (\hat{c}_k^\dagger + \hat{c}_k), \] (A.1)

\[ \hat{p}_k = i\sqrt{\frac{\nu_k}{2}} (\hat{c}_k^\dagger - \hat{c}_k), \] (A.2)

and associating them with classical coordinates \( \hat{x}_k \rightarrow x_k(t) \) and \( \hat{p}_k \rightarrow p_k(t) \). We also replace the TLS with a continuous variable \( q(t) \) subject to a potential \( V(q) \). We furthermore map the TLS-bath interaction and bath energy to a quadratic potential, such that the classical Hamiltonian for the spin-boson system is given by,

\[ H_{SB}^q = \frac{1}{2} P_q(t)^2 + V(q) + \frac{1}{2} \sum_k p_k(t)^2 + \frac{1}{2} \sum_k \left( \frac{\tilde{f}_k q(t) + \nu_k x_k(t)}{\nu_k^2} \right)^2 \] (A.3)

\[ = \frac{1}{2} P_q(t)^2 + V(q) + q(t) \sum_k \tilde{f}_k x_k(t) + q(t)^2 \sum_k \frac{\tilde{f}_k^2}{2\nu_k^2} + \frac{1}{2} \sum_k (p_k(t)^2 + \nu_k^2 x_k(t)^2), \] (A.4)
where \( \tilde{f}_k = \sqrt{2\nu_k} f_k \). Now we can use Hamilton’s equations for each coordinate:

\[
\begin{align*}
\text{TLS} & \quad \left\{ \begin{array}{l}
\dot{q}(t) = \frac{\partial H_{\text{TLS}}}{\partial p_q} = P_q \\
\dot{P}_q(t) = \ddot{q} = -\frac{\partial H_{\text{TLS}}}{\partial q} = -V'(q) - \sum_k \tilde{f}_k x_k(t) - q(t) \sum_k \frac{\tilde{f}_k^2}{\nu_k},
\end{array} \right. \\
\text{Bath} & \quad \left\{ \begin{array}{l}
\dot{x}_k = \frac{\partial H_{\text{TLS}}}{\partial p_k} = p_k \\
\dot{p}_k = -\frac{\partial H_{\text{TLS}}}{\partial x_k} = -q(t) \tilde{f}_k - \nu_k^2 x_k(t).
\end{array} \right.
\]

(A.5)

Applying the Fourier transform \( \mathcal{F}[h(t)](z) = \tilde{h}(z) = \int_{-\infty}^{\infty} h(t) e^{-izt} dt \) to Eqs. (A.5) and (A.6) we obtain the transformed equations,

\[
\begin{align*}
-z^2 \tilde{q}(z) &= -\tilde{V}'(q) - \sum_k \tilde{f}_k \tilde{x}_k(z) - \tilde{q}(z) \sum_k \frac{\tilde{f}_k^2}{\nu_k^2}, \\
-z^2 \tilde{x}_k(z) &= -\tilde{q}(z) \tilde{f}_k - \nu_k^2 \tilde{x}_k(z).
\end{align*}

(A.7)

We can eliminate the bath coordinates by combining the above equations to get an equation of the form \( \tilde{K}(z) \tilde{q}(z) = -\tilde{V}'(q) \), where

\[
\tilde{K}(z) = -z^2 \left( 1 + \sum_k \frac{\tilde{f}_k^2}{\nu_k^2} \right) = -z^2 \left( 1 + \int_0^\infty \frac{J_{\text{SB}}(\nu)}{\nu(\nu^2 - z^2)} d\nu \right).
\]

(A.9)

Using results from Refs. [10, 27] we can express the spin-boson spectral density in terms of \( \tilde{K}(z) \):

\[
J_{\text{SB}}(\omega) = \frac{1}{\pi} \lim_{\varepsilon \to 0^+} \left[ \tilde{K}(\omega - i\varepsilon) \right].
\]

(A.10)

Next, we apply the same procedure for the reaction coordinate Hamiltonian, assigning to the reaction coordinate the classical coordinates \( y(t) \) and \( P_y(t) \). We further assume that for a fixed \( q(t) \), the reaction coordinate follows a quadratic potential of the form

\[
\frac{1}{2} \Omega^2 \left[ y(t) + \frac{\kappa}{\Omega^2} q(t) \right]^2,
\]

(A.11)

so that the coordinate \( y(t) \) will satisfy the classical equation of motion describing a system with Ohmic spectral density [12]. We now have the classical Hamiltonian for the RC system:

\[
H_y^{\text{RC}} = \frac{1}{2} P_y(t)^2 + V(q) + \kappa q(t) g(t) + \frac{\kappa^2}{2\Omega^2} q(t)^2 + \frac{1}{2} [P_y(t)^2 + \Omega^2 y(t)^2]
+ y(t) \sum_k \dot{g}_k X_k(t) + y(t)^2 \sum_k \frac{\dot{g}_k^2}{2\omega_k^2} + \frac{1}{2} \sum_k \left[ P_k(t)^2 + \omega_k^2 X_k(t)^2 \right],
\]

(A.12)
where \( \kappa = \sqrt{2\Omega\lambda} \), \( \tilde{g}_k = 2\sqrt{\Omega\omega_k}g_k \), and \( X_k(t) \), \( P_k(t) \) are the positions and momentums of the \( k \)-th residual bath oscillator, respectively.

Again, applying Hamilton’s equations to the reaction coordinate Hamiltonian we get the equations of motion:

\[
\begin{align*}
\text{TLS} \quad & \quad \dot{q}(t) = \frac{\partial H_{RC}^q}{\partial P_q} = P_q \quad (A.13) \\
\quad & \quad \dot{P}_q(t) = \ddot{q} = -\frac{\partial H_{SB}^q}{\partial q} = -V'(q) - \kappa y(t) - \frac{\kappa^2}{\Omega^2}q(t), \\
\text{RC} \quad & \quad \dot{y}(t) = \frac{\partial H_{RC}^y}{\partial P_y} = P_y \quad (A.14) \\
\quad & \quad \dot{P}_y(t) = \ddot{y} = -\frac{\partial H_{SB}^y}{\partial y} = -\kappa q(t) - \Omega^2 y(t) - \sum_k \tilde{g}_k X_k(t) - y(t) \sum_k \frac{\tilde{g}_k^2}{\omega_k^2}, \\
\text{Bath} \quad & \quad \dot{X}_k = \frac{\partial H_{RC}^{X_k}}{\partial P_k} = P_k \quad (A.15) \\
\quad & \quad \dot{P}_k = \ddot{X}_k = -\frac{\partial H_{SB}^{X_k}}{\partial X_k} = -y(t)\tilde{g}_k - \omega_k^2 X_k(t).
\end{align*}
\]

As before, we transform the above equations of motion into Fourier space to get equations of the form

\[
\begin{align*}
-\hat{z}^2\hat{q}(z) &= -V'(q) - \kappa \hat{y}(z) - \frac{\kappa^2}{\Omega^2} \hat{q}(z), \quad (A.16) \\
-\hat{z}^2\hat{y}(z) &= -\kappa \hat{q}(z) - \sum_k \tilde{g}_k \hat{X}_k(z) - \hat{y}(z) \sum_k \frac{\tilde{g}_k^2}{\omega_k^2}, \quad (A.17) \\
-\hat{z}^2\hat{X}_k &= -\tilde{g}_k \hat{y}(z) - \omega_k^2 \hat{X}_k. \quad (A.18)
\end{align*}
\]

After some algebra, we can show that

\[
[\mathcal{L}(z) + \Omega^2]\hat{y}(z) = -\kappa \hat{q}(z), \quad (A.19)
\]

and

\[
\tilde{K}(z)\hat{q}(z) = -V'(q), \quad (A.20)
\]

where \( \mathcal{L}(z) \) and \( \tilde{K}(z) \) are given by

\[
\begin{align*}
\mathcal{L}(z) &= -z^2 \left[ 1 + \sum_k \frac{\tilde{g}_k^2}{\omega_k^2(\omega_k^2 - z^2)} \right] = -z^2 \left[ 1 + 4\Omega \int_0^\infty \frac{J_{RC}(\omega)}{\omega(\omega^2 - z^2)} \, d\omega \right], \quad (A.21) \\
\tilde{K}(z) &= -z^2 + \frac{\kappa^2}{\Omega^2} \frac{\mathcal{L}(z)}{\Omega^2 + \mathcal{L}(z)}. \quad (A.22)
\end{align*}
\]

Using the Ohmic spectral density \( J_{RC}(\omega) = \gamma \omega e^{-\omega/\Lambda} \) in Eq. (A.21), and taking the
limit $\Lambda \to \infty$ to make the integral tractable, we simplify $\mathcal{L}(z)$ to

$$\mathcal{L}(z) = -z^2 + i2\pi\gamma z.$$  \hspace{1cm} (A.23)

Substituting this result into Eq. (A.22) we can apply the Leggett prescription [10,12]:

$$J_{SB}(\omega) = \lim_{\varepsilon \to 0^+} \frac{1}{\pi} \text{Im} \left[ \tilde{K}(\omega - i\varepsilon) \right]$$

$$= \frac{1}{\pi} \frac{2\pi\gamma\kappa^2\omega}{\left(\Omega^2 - \omega^2\right)^2 + (2\pi\gamma\Omega^2)^2},$$

(A.24) \hspace{1cm} (A.25)

giving us the spectral density distribution in the spin-boson model.
Appendix B

Eigenstates of a general two-level system

We consider a two-level system described by a Hamiltonian

\[ \hat{H}_{TLS} = \frac{\varepsilon}{2} \hat{\sigma}_z + \frac{\Delta}{2} \hat{\sigma}_x, \]  

where \( \hat{\sigma}_z = |1\rangle \langle 1| - |2\rangle \langle 2| \) and \( \hat{\sigma}_x = |1\rangle \langle 2| - |2\rangle \langle 1| \). In the representation

\[ |1\rangle \equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \]  

and

\[ |2\rangle \equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \]

\( \hat{H}_{TLS} \) assumes a matrix representation

\[ H_{TLS} = \frac{1}{2} \begin{pmatrix} \varepsilon & \Delta \\ \Delta & -\varepsilon \end{pmatrix}. \]

We will also denote the ground and excited states of the TLS by \( |g\rangle \) and \( |e\rangle \), respectively, with the associated vector representations \( v_g \) and \( v_e \). Let us solve for the
eigenvalues \{\lambda_+, \lambda_-\} of \(H_{\text{TLS}}\) with the help of
\[
0 = \det (H_{\text{TLS}} - \lambda I_{\text{TLS}}) = \det \begin{pmatrix} \frac{\varepsilon}{2} - \lambda & \frac{\Delta}{2} \\ \frac{\Delta}{2} & -\frac{\varepsilon}{2} - \lambda \end{pmatrix} = \lambda^2 - \frac{1}{4}(\varepsilon^2 + \Delta^2).
\]
Thus the eigenvalues are given by
\[
\lambda_{\pm} = \pm \frac{1}{2}\sqrt{\varepsilon^2 + \Delta^2}.
\]
We identify \(\lambda_g \equiv \lambda_-\) for the ground state energy, and \(\lambda_e \equiv \lambda_+\) for the excited state energy. Using these eigenvalues we can calculate the eigenvectors as follows:
\[
H_{\text{TLS}}v_e = \lambda_e v_e
\]
\[
\frac{1}{2} \begin{pmatrix} \varepsilon & \Delta \\ \Delta & -\varepsilon \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \frac{1}{2} \begin{pmatrix} \sqrt{\varepsilon^2 + \Delta^2}a \\ b \end{pmatrix}
\]
\[
\begin{pmatrix} \varepsilon a + \Delta b \\ \Delta a - \varepsilon b \end{pmatrix} = \begin{pmatrix} \sqrt{\varepsilon^2 + \Delta^2}a \\ \sqrt{\varepsilon^2 + \Delta^2}b \end{pmatrix},
\]
where the equality of the first components gives us that
\[
b = \frac{\sqrt{\varepsilon^2 + \Delta^2} - \varepsilon}{\Delta}a.
\]
At this point, it is convenient to introduce the following notation:
\[
\cos(\theta) = \frac{\varepsilon}{\sqrt{\varepsilon^2 + \Delta^2}},
\]
\[
\sin(\theta) = \frac{\Delta}{\sqrt{\varepsilon^2 + \Delta^2}},
\]
so that the normalization condition $\|v_e\| = 1$ yields

$$1 = |a|^2 + |b|^2 = |a|^2 + \left( \frac{\sqrt{\varepsilon^2 + \Delta^2} - \varepsilon}{\Delta} \right)^2 |a|^2 = |a|^2 + \left( \frac{\sqrt{\varepsilon^2 + \Delta^2} - \varepsilon}{\Delta} \right)^2 |a|^2$$

$$= |a|^2 + \left( \frac{1}{\sin(\theta)} - \frac{\cos(\theta)}{\sin(\theta)} \right)^2 |a|^2 = |a|^2 + \left( \frac{1 - \cos(\theta)}{\sin(\theta)} \right)^2 |a|^2$$

$$= |a|^2 \left( \frac{\sin^2(\theta) + 1 + \cos^2(\theta) - 2\cos(\theta)}{\sin^2(\theta)} \right) = |a|^2 \left( \frac{2 - 2\cos(\theta)}{\sin^2(\theta)} \right)$$

$$= 2|a|^2 \left( \frac{1 - \cos(\theta)}{(1 - \cos(\theta))(1 + \cos(\theta))} \right)$$

$$= 2|a|^2 \frac{1}{1 + \cos(\theta)},$$

and hence

$$|a|^2 = \frac{1}{2} [1 + \cos(\theta)] = \cos^2 \left( \frac{\theta}{2} \right). \quad \text{(B.15)}$$

Subsequently we express $a$ in the form,

$$a = e^{i\phi_1} \cos \left( \frac{\theta}{2} \right), \quad \text{(B.16)}$$

where $e^{i\phi_1}$ is some phase factor. We also obtain

$$|b|^2 = 1 - |a|^2 = \sin^2 \left( \frac{\theta}{2} \right),$$

implying that

$$b = e^{i\phi_2} \sin \left( \frac{\theta}{2} \right). \quad \text{(B.17)}$$

From (B.12) we see that the phase factors $\phi_1$ and $\phi_2$ must be equal — let’s call it $\phi$. Using (B.16) and (B.17) we have that

$$v_e = \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} e^{i\phi} \cos \left( \frac{\theta}{2} \right) \\ e^{i\phi} \sin \left( \frac{\theta}{2} \right) \end{pmatrix} = e^{i\phi} \begin{pmatrix} \cos \left( \frac{\theta}{2} \right) \\ \sin \left( \frac{\theta}{2} \right) \end{pmatrix}. \quad \text{(B.18)}$$

Dropping the global phase factor we arrive at the eigenvector for the excited state,

$$v_e = \begin{pmatrix} \cos \left( \frac{\theta}{2} \right) \\ \sin \left( \frac{\theta}{2} \right) \end{pmatrix} = \cos \left( \frac{\theta}{2} \right) |1\rangle + \sin \left( \frac{\theta}{2} \right) |2\rangle. \quad \text{(B.19)}$$
A similar calculation will show that the eigenvector for the ground state is given by,

\[ v_g = \begin{pmatrix} -\sin\left(\frac{\theta}{2}\right) \\ \cos\left(\frac{\theta}{2}\right) \end{pmatrix} = -\sin\left(\frac{\theta}{2}\right) |1\rangle + \cos\left(\frac{\theta}{2}\right) |2\rangle. \]  

(B.20)

Using Eqs. (B.13) and (B.14), and the equalities

\[ \cos^2\left(\frac{\theta}{2}\right) = \frac{1}{2} [1 + \cos(\theta)], \]  

(B.21)

\[ \sin^2\left(\frac{\theta}{2}\right) = \frac{1}{2} [1 - \cos(\theta)], \]  

(B.22)

we can express the components of the eigenvectors in terms of the parameters \( \varepsilon \) and \( \Delta \) as

\[ \cos\left(\frac{\theta}{2}\right) = \sqrt{\frac{\sqrt{\varepsilon^2 + \Delta^2} + \varepsilon}{2\sqrt{\varepsilon^2 + \Delta^2}}}, \]  

(B.23)

\[ \sin\left(\frac{\theta}{2}\right) = \sqrt{\frac{\sqrt{\varepsilon^2 + \Delta^2} - \varepsilon}{2\sqrt{\varepsilon^2 + \Delta^2}}}. \]  

(B.24)
Appendix C

Expectation value of bath operator $\hat{B}_I(t)$ in the Gibbs state

We wish to show that the expectation value of the bath operator $\hat{B}_I(t)$ with respect to the Gibbs state $\hat{\rho}_B$ is zero. This can be shown quickly by choosing our basis to be the Fock states for a bosonic bath,

$$|\{n_k\}⟩ = |n_1, n_2, \ldots, n_\ell, \ldots⟩,$$

which have the following properties:

$$\hat{b}_k^\dagger |n_1, n_2, \ldots, n_k, \ldots⟩ = \sqrt{n_k + 1} |n_1, n_2, \ldots, n_k + 1, \ldots⟩,$$  \hspace{1cm} (C.2)

$$\hat{b}_k |n_1, n_2, \ldots, n_k, \ldots⟩ = \sqrt{n_k} |n_1, n_2, \ldots, n_k - 1, \ldots⟩.$$  \hspace{1cm} (C.3)

From the above relations it follows that $\hat{b}_k^\dagger \hat{b}_k |\{n_k\}⟩ = n_k |\{n_k\}⟩$, and since $H_B = \sum_k \hbar \omega_k \hat{b}_k^\dagger \hat{b}_k$, the expectation value of $\hat{B}_I(t)$ can be expressed in the form

$$\langle \hat{B}_I(t) \rangle_{\hat{\rho}_B} = \text{Tr} \left[ \hat{B}_I(t) \hat{\rho}_B \right] = \frac{1}{Z} \sum_{\{n_k\}} \langle \{n_k\} | e^{i\hat{H}_B t/\hbar} \hat{B} e^{-i\hat{H}_B t/\hbar} e^{-\beta \hat{H}_B} |\{n_k\}⟩$$

$$= \frac{1}{Z} \sum_{\{n_k\}} e^{-\beta \sum_k \omega_k n_k} \langle \{n_k\} | \hat{B} |\{n_k\}⟩,$$

where $\sum_{\{n_k\}} = \sum_{n_1} \sum_{n_2} \cdots \sum_{n_\ell} \cdots$, and $Z = \text{Tr}(e^{-\beta \hat{H}_B})$. Since $\hat{B} = \sum_\ell g_\ell (\hat{b}_\ell^\dagger + \hat{b}_\ell)$ and $\langle \{n_k\} | \hat{b}_\ell^\dagger |\{n_k\}⟩ = \langle \{n_k\} | \hat{b}_\ell |\{n_k\}⟩ = 0$ for all $n_k$ and $\ell$, it follows that $\langle \hat{B}_I(t) \rangle_{\hat{\rho}_B} = 0$. 

61
Appendix D

Integration by parts of dissipation term

Here we prove the equality in Eq. (3.53) using integration by parts and the continuum form of the Ohmic spectral density, to show that

\[
\int_0^\infty \int_0^\infty d\tau d\omega J_{RC}(\omega) \sin(\omega \tau) \hat{A}_I(t - \tau) \hat{A}_I(t) = \int_0^\infty d\omega J_{RC}(\omega) \frac{\hat{A}_I(t)}{\omega} + \int_0^\infty \int_0^\infty d\tau d\omega J_{RC}(\omega) \frac{\cos(\omega \tau)}{\omega} \frac{\partial \hat{A}_I(t - \tau)}{\partial \tau}. \quad (D.1)
\]

We begin by using integration by parts with respect to the integral over \(\tau\) by letting \(u = \hat{A}_I(t - \tau)\) and \(dv = \sin(\omega \tau) d\tau\), so that \(du = \frac{\partial \hat{A}_I(t - \tau)}{\partial \tau} d\tau\) and \(v = -\frac{\cos(\omega \tau)}{\omega}\), such that the integral becomes

\[
\int_0^\infty \int_0^\infty d\omega J_{RC}(\omega) \int_0^\infty d\tau \sin(\omega \tau) \hat{A}_I(t - \tau) = \int_0^\infty d\omega J_{RC}(\omega) \left( uv \bigg|_{\tau=0}^{\tau=\infty} - \int_0^\infty v du \right)
\]

\[
= \int_0^\infty d\omega J_{RC}(\omega) \left[ -\frac{\cos(\omega \tau)\hat{A}_I(t - \tau)}{\omega} \right]_{\tau=0}^{\tau=\infty} + \int_0^\infty d\omega J_{RC}(\omega) \int_0^\infty \left( \frac{\cos(\omega \tau)}{\omega} \right) \frac{\partial \hat{A}_I(t - \tau)}{\partial \tau} d\tau \quad (D.2)
\]

The last line of the above equation is already in the desired form. To evaluate the integral over \(\omega\) of the limit term in Eq. (D.2), we first evaluate the limits inside the integral to get

\[
\int_0^\infty d\omega J_{RC}(\omega) \left[ \frac{\hat{A}_I(t)}{\omega} - \lim_{\tau \to \infty} \left( \frac{\cos(\omega \tau)\hat{A}_I(t - \tau)}{\omega} \right) \right], \quad (D.3)
\]

63
where we see that the term on the left side of the argument is what we desire for the final result. To argue that the limit term on the right must vanish, we consider the Ohmic spectral density $J_{RC}(\omega) = \gamma \omega e^{-\omega / \Lambda}$ and note that $\cos(\omega \tau) = \Re(e^{i \omega \tau})$, so that

$$\int_0^\infty d\omega J_{RC}(\omega) \lim_{\tau \to \infty} \left( \frac{\cos(\omega \tau) \hat{A}_1(t-\tau)}{\omega} \right) = \gamma \lim_{\tau \to \infty} \hat{A}_1(t-\tau) \Re \int_0^\infty d\omega \frac{\omega e^{-\omega / \Lambda} e^{i \omega \tau}}{\omega}.$$  \hspace{1cm} (D.4)

Taking only the integral term from above we have

$$\Re \int_0^\infty d\omega e^{(i \tau - 1 / \Lambda) \omega} = \Re \left[ \frac{1}{i \tau - 1 / \Lambda} e^{(i \tau - 1 / \Lambda) \omega} \right]_{\omega = 0} \bigg|_{\omega = \infty}. \hspace{1cm} (D.5)$$

For all $\Lambda > 0$ the upper limit $\omega \to \infty$ will go to zero in the above term. Furthermore, in the limit $\tau \to \infty$ the lower bound will go to zero also, and hence we can write the claimed result.