# THERMALIZATION OF A CAVITY MODE IN THE PRESENCE OF A DYE MOLECULE

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David Wierichs: *Thermalization of a Cavity Mode in the Presence of a Dye Molecule,* © November 2018 Dedicated to its readers. This would not be reasonable without you.

Understanding the dynamical behaviour of quantum mechanical many-particle systems comes with a wide range of challenges to which mutually compatible answers have to be given. For the investigations in this thesis, the framework of Open Quantum Systems is found to be particularily useful, matching several of our interests such as a detailed description of a small part of a fairly large system, a far-developed set of approximative schemes in order to arrive at models of manageable complexity and the possibility to implement the theory on the computer for numerical evaluation. The separation of the system introduces distinct time scales for the dynamics of the two subsystems and the split up corresponds to the physical understanding of a system weakly coupled to a second one which has perturbative effects on the former. Due to this approach, the entire time evolution is described in the reduced Hilbert space. In conclusion, we want to employ this theory for our project and review its results and methods.

Before employing the existing toolset of Open Quantum System theory, this thesis first documents the derivation process for commonly employed effective descriptions in this framework and approximative schemes therein. After all, the numerical implementation of the full system requires a discretized representation of the infinite bath. Therefore, this topic is reviewed and several strategies, including recent proposals, are evaluated numerically regarding their precision and the size of the resulting bath that is required for the representation. In summary the investigated topics include the Markov, the secular and the weak-coupling approximation, bath discretization as mentioned above and aspects of physicality of mathematical descriptions of the original system as well as experimentally measured spectra of molecular rovibrational baths. We find interesting results on the various methods to mimic an infinite (or continuous) environment, which call for further investigations on this topic. Further, we are able to demonstrate effects of the approximations of the master equation, including temperature-dependent long-time behaviour of the secular approximation and its possible unphysicality for specific systems, the failure of the Markovian description for systems with short-time dynamics and the deviation introduced by explicitly employing the weak-coupling approximation.

As second core part, this project looks at methods to evaluate the results given by the Open Quantum System theory, treating the analytically solvable spin-boson-model and realizing the systems of interest with the numerically exact Density Matrix Renormalization Group concept.

First of all, the new discretization scheme is rated and found to give improved characteristics of the finite bath in comparison to a linearly sampled bath.

For the reduced system case, i. e. the spin-boson-model, we find the master equation within the Open Quantum System (OQS) framework to describe the time evolution well in the dephasing limit, with deviations from the exact solution in reasonable relation to the employed approximations. For cases away from the pure dephasing limit, we find the non-secular master equation to describe the numerically exact dynamics very well for long times, predicting the approached state correctly, whereas short-time behaviour and details of the evolution are poorly reproduced by the Master Equation (ME). Finally, for the full system and the dephasing configuration of the spin, we find the spin dynamics to be disturbed by interactions with the cavity mode. The cavity on the other hand is observed to approach a (quasi-)stationary state which is not the thermal state for the cavity alone. We connect this non-thermalizing behaviour to the conservation of the particle number in the specific system and observe an interesting dependency of the coherences in the OQS on the bath temperature, resulting in seemingly stationary states of the system for large temperatures and in fluctuating states with stationarity only in the system energies but not in the coherences for lower temperatures. Likewise, the entire OQS does not thermalize due to the dephasing configuration of the spin, which limits the energy flow between the open system and the bath and fixes the occupation number.

In summary, we were able to give an overview of the various approximations in the master equation, partially with interesting results that call for careful analysis of a system before employing these common methods. In future works our setup can be used to compute the full system with increased complexity, i. e. for the spin Hamiltonian away from the dephasing configuration and for strong couplings. Furthermore, by translating the weak-coupling bond, we can investigate the cavity mode in presence of the dye molecule as an anharmonic bath, connecting to multiple recent research projects [23, 28, 29]. CONTENTS

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## ACRONYMS

DMRG Density Matrix Renormalization Group

- OQS Open Quantum System
- ME Master Equation
- MME Markovian Master Equation
- nMME non-Markovian Master Equation
- DOS Density Of States
- DOF Degree Of Freedom
- TDVP Time-Dependent Variational Principle
- FWHM Full Width at Half Maximum
- HWHM Half Width at Half Maximum
- MPS Matrix Product State
- MPO Matrix Product Operator
- SVD Singular Value Decomposition

In this thesis, we analyze the time evolution of composite systems which combine electromagnetic fields, molecular vibrations and electronic degrees of freedom. We specifically treat a cavity containing a single electromagnetic mode which interacts with a molecule, typically chosen to be a dye molecule in experimental setups. As an initial motivation for our work we first introduce the physical system on the basis of established experimental setups and discuss interesting observations that have been made. The theoretical description of the system and the transition towards a finite-size model is presented below in chapter 2.

An illustration of the system is shown in fig. 1.1, displaying the



Figure 1.1: Scheme of the physical system of interest for our project: An electromagnetic field enclosed in a cavity in the presence of a single dye molecule; The relation of this setup to real-world experiments is described in the text. Figure adapted from [36].

cavity that contains an electromagnetic field with a single mode and showing a single molecule. The respective real experimental setup differs significantly in size as typically a solution containing a huge number of molecules is considered instead and the electromagnetic cavity contains a whole range of modes [29, 30].<sup>1</sup> Still our work is potentially able to lead towards an understanding of the dynamics of such bigger systems. On one hand, the simpler setup here analyzed will allow us to study the regime of validity of the approximations used for the analysis of the larger system containing many molecules. Furthermore, effects present in the big system which originate from the single-molecule dynamics can be described, which is a reasonable idea because in such setups we consider a diluted sample of dye molecules with neglegible direct interaction. On the other hand, one can argue that the resonant two-level transition will be most relevant and that thus our single-molecule system is a good starting point for

<sup>1</sup> However, it is indeed possible to set the system up as presented here, injecting a single dye molecule into a cavity. [49]

the investigation of the full real-world system.

The motivation to understand the time evolution of our system can be given on the basis of different insights made recently in both, experiments and theoretical investigations. The first motivation we want to give here is related to a result of Klaers et al.[29, 30], which shows thermalization of the electromagnetic field within the cavity, based on the interaction with dye molecules. Although there has been theoretical work on the phenomenon of the photonic thermalization and its breakdown [28], our work might provide new insights on how to understand the time evolution of the system as the existing work focuses on steady state solutions. Such steady states are associated to different "phases" of the photon gas and depend on certain parameters such as the cavity size or the vibrational degrees of freedom of the dye molecules. The similarity of the experiments of interest to standard laser setups is another interesting aspect of the presented system.

A second core result - this time of theoretical origin - is found in [23] and deals with the behaviour of a two-level system (or spin) in presence of two different environments. In the case of the environment being harmonic, an increased decoherence rate for the spin can be observed when increasing the temperature of the bath, whereas the setup with an anharmonic bath - realized by inserting a mediating two-level system between spin and bath - exhibits the astonishing feature of decreased decoherence rates for increased temperatures of the bath. The molecule in our system - as it is a combination of two-level system and bosonic modes - exactly realizes such an anharmonic bath, providing us with a connection to the above insights. Although being interesting on its own because of its counter-intuitivity, the result might additionally enable future experiments to observe quantum physics under significantly less strict contraints, as decoherence can be understood as "decay of quantumness" of a system or its state. Due to high coherence requirements in quantum computing setups, the result is even more interesting as it possibly could lead to relaxed constraints on the cooling of such experiments and therefore facilitate the realization of bigger systems and actually operable computing setups. Therefore, understanding the mentioned result in detail and investigating the behaviour of a bosonic mode in presence of an anharmonic bath, as provided by the dye molecule, is interesting from both a theoretical and an experimental perspective. This thesis establishes the models and methods towards such an understanding and provides the necessary numerical implementations, but we want to mention, that within this project, we do not cover the corresponding split up of our system (by means of a weak-coupling bond) yet.

After having motivated our work by the above results from the past ten years, we want to conclude which framework is suitable for our goals. Our investigation focuses on the dynamical behaviour of the bosonic mode and the two-level system incorporated in the dye molecule. Meanwhile, the details of the other degrees of freedom of the molecule - we consider them to be of rovibrational nature and describe them as harmonic - are of lesser importance to us. It therefore is reasonable to choose a theory which is able to differentiate between parts of the system in a corresponding manner, paying reduced attention to a large part of the system. This leads us to the theory of open quantum systems, which is widely used in quantum optics [20, 41], condensed matter physics [4, 15] and quantum computing [2, 3, 27], amongst others. The separation into a small system which is investigated closely and an environment or bath which is taken into account as an effective influence on that small system exactly matches our preferences and as there have been established both, rigorous proofs of desirable properties of the theory and practical application and approximation schemes, we have a proper set of tools and knowledge at hand for our work within this framework. In particular, the *master equation* and its approximation schemes and mathematical properties will play a central role for our project.

In addition to the open quantum systems theory, we will employ highly developed numerical tools to analyze the time evolution of the considered system on a numerically exact level, enabling us to evaluate results of the master equation, which includes a whole range of approximations and corresponding assumptions, on one hand and providing a fundamentally different setup of investigation in order to gain a diversified view on the matter on the other hand.

In addition to the above motivation regarding research, we want to state that this thesis of course also fulfils educational purpose for the author. It therefore contains summaries of relevant aspects to our work, such as the topic of bath discretization and approximation schemes in the OQS theory, which contain lesser amounts of new results (although not none) but mainly serve as a review and introduction to the main part. As the reader might notice, these "prerequisites" form a major part of the present thesis, which reflects the progress throughout the project and the time and effort spend on particular topics.

#### Part I

## GOOD TO KNOW

The first main part of the thesis contains a whole range of preliminary topics and introductory reviews. Although it does not consist of major new research, relevant questions to our project are answered and common notions are applied to our case, going through some of the standard procedures in a more critical way and testing some of them numerically.

In chapter 2 we first clarify the notational conventions and establish the mathematical models for the system introduced in chapter 1, leading us to the challenge of the infinite to finite bath conversion, which is tackled in chapter 3. Following up, we review the weak-coupling master equation and its derivation in chapter 4, paying particular attention to approximation schemes and assumptions linked to them, including some evaluation of their practicality and applicability to describe truely physical systems. Finally we include a brief introduction to the Density Matrix Renormalization Group (DMRG) in chapter 5 where we establish the needed notions for our work and connect them to standard literature but also discuss the application of the more specific technique of purification to our model as we will need it to realize thermal states.

This chapter presents the theoretical description of the physical system introduced in chapter 1 and establishes some standard notation used troughout the entire thesis.

We start with the full system Hamiltonian H which can be split up in three parts, corresponding to the open quantum system (H<sub>S</sub>), the bath (H<sub>B</sub>), also referred to as environment, and the interaction of these two subsystems (H<sub>I</sub>). We denote the standard time evolution operators as U(t) and U<sub>0</sub>(t) for the full Hamiltonian and the interaction-free part of H, respectively. For convenience we will not write out the time evolution by preceding and trailing U's but write the (interaction-free) time evolution of an operator using the superoperator V<sub>t</sub> which is understood to act on *one* single operator to the right corresponding to  $U_0^{\dagger} \cdot U_0$ . We summarize the basic notation as

$$\begin{array}{lll} H = H_0 + H_I & ; & H_0 = H_S + H_B & (2.1) \\ U(t) = e^{-itH} & ; & U_0(t) = e^{-itH_0} & ; & V_tO = U_0^{\dagger}(t) \, O \, U_0(t) \end{array}$$

Together with the separation of the system Hilbert space into two subspaces, we can introduce the partial trace. It acts on the bath part of an operator only and is denoted by  $tr_B \{\cdot\}$  while  $tr \{\cdot\}$  denotes the trace over all dimensions of an operator that is we write

$$tr\{O\} tr\{O_S\} tr\{O_B\}$$
 (2.2)

for an operator O on the full system and subsystem operators  $O_{S/B}$  on the OQS part or the bath space respectively.

As is common in theoretical physics, we will abuse the notation with respect to the Hilbert spaces on which operators act, meaning that we will omit tensor factors of  $\mathbb{1}_S$  or  $\mathbb{1}_B$  for notational convenience. This convention demands a certain amount of trust by the reader in the proper mathematical treatment behind the results, which we shall assume for our project. One consequence of the reduced notation is that the expressions  $V_tO_S$  and  $V_tO_B$  for an arbitrary OQS or bath space operator respectively are well-defined and make sense, evaluating to

$$V_tO_S = e^{itH_S}O_Se^{-itH_S}$$
 and  $V_tO_B = e^{itH_B}O_Se^{-itH_B}$ .

We will furthermore denote the density matrix of our full system by  $\rho$  whereas the reduced density matrix of the OQS alone is written as  $\rho_S = \text{tr}_B \{\rho\}$ . For as long as it is feasible, we will keep results general before applying them to our concrete system (see below). In

this context, we want to introduce one further notation regarding the interaction Hamiltonian  $H_I$  and write it in the form

$$H_{I} = \mathcal{A} \otimes \mathcal{B} \tag{2.3}$$

with open system operator  $\mathcal{A}$  and bath operator  $\mathcal{B}$ , both of which are required to be Hermitian. In the most general setting, there is a collection of these operators, but as our examples can be formulated in terms of one operator for the OQS and the environment each, we will stay in this restricted setting.

After having shown the general framework we are considering, we now turn to the concrete exemplary systems investigated in this thesis. We will choose the bath to be bosonic and interaction free, i.e. to consist of harmonic oscillators which are not coupled to each other. We elaborate on the distinction between an infinite and a finite bath in chapter 3 and for now consider infinitely many discrete modes. The bath models the rovibrational Degrees Of Freedom (DOFs) of the dye molecule as described in chapter 1. Furthermore, the OQS consists of the cavity mode, modelled as simple harmonic oscillator as well, and the electronic two-level system of the dye molecule, represented by a standard spin DOF and referred to as spin, two-level system or dye. The combination of cavity and spin is then linearly coupled to the bath via the two-level system and in a star configuration. This means that the bath component of  $H_I$ ,  $\mathcal{B}$ , is proportional to all the harmonic oscillator positions  $\{x_k = b_k^{\dagger} + b_k\}_{k}$ , including a coupling prefactor, and the system component A is a non-trivial operator on the spin part only. In other words, the spin interacts with the bath in a typical electronic-phononic coupling manner. The internal interaction of the OQS is excitation-preserving w.r.t. the particle number basis of the cavity and the  $\sigma_z$ -basis of the spin.<sup>1</sup> In symbols, our system Hamiltonian is [28]

$$\begin{split} H_{S} &= \omega_{C} a^{\dagger} a + \frac{\omega_{S}}{2} \sigma_{z} + \frac{\Delta}{2} \sigma_{x} + g(a^{\dagger} \sigma^{-} + a \sigma^{+}) \\ Full System \quad H_{B} &= \sum_{k=1}^{\infty} \Omega_{k} b_{k}^{\dagger} b_{k} \\ H_{I} &= \sigma_{z} \sum_{k=1}^{\infty} \tilde{g}_{k} (b_{k}^{\dagger} + b_{k}) \end{split}$$
(2.4)

where  $\omega_{\rm C}$ ,  $\omega_{\rm S}$  and  $\Delta$  are the energies of the cavity mode and of the *z*- and the x-direction excitations of the dye molecule, g is the coupling parameter between the cavity and the spin,  $\Omega_{\rm k}$  denotes the k-th bath mode energy and  $\tilde{g}_{\rm k}$  stands for the corresponding coupling coefficient between bath mode k and the spin. The used operators are the raising and lowering operators of the harmonic mode,  $a^{\dagger}$ 

<sup>1</sup> Note that with the transition from the physical to the theoretical system the notion of "internal" changed from the link spin-bath to the link cavity-spin.

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and a, the creation and annihilation operators for spin excitations,  $\sigma^+$  and  $\sigma^-$ , and the *z*- and x-direction spin operators defined by  $\sigma_x = \sigma^+ + \sigma^-$  and  $\sigma_z = \sigma^+ \sigma^- - \sigma^- \sigma^+$ . Finally,  $b_k^{\dagger}$  and  $b_k$  denote the bosonic bath raising and lowering operators. For convenience, we will sometimes abbreviate  $B = \sum_{k=1}^{\infty} \tilde{g}_k b_k$  and as mentioned above we have  $\mathcal{B} = B^{\dagger} + B$  as well as  $\mathcal{A} = \sigma_z$ .

For benchmarking purposes and in order to establish some basic concepts and phenomena, we will also use a second model which is a subsystem of the above, leaving out the cavity mode and thus reducing the open quantum system to a single spin. This minor version of the system is known as spin-boson model (c. f. chapter 6) and we will be able to make use of well-known results for this easier case. Again we write it out symbolically as

$$\begin{split} H_{S} &= \frac{\omega_{S}}{2}\sigma_{z} + \frac{\Delta}{2}\sigma_{x} \\ \text{Spin-Boson Model} \quad H_{B} &= \sum_{k=1}^{\infty} \Omega_{k}b_{k}^{\dagger}b_{k} \\ H_{I} &= \sigma_{z}\sum_{k=1}^{\infty} \tilde{g}_{k}(b_{k}^{\dagger} + b_{k}) \end{split}$$
(2.5)

Obviously, the transition from the full system to this smaller one can be performed by setting g to 0 and ignoring the cavity part. Throughout the whole project the bath will be assumed to be in a thermal initial state, and depending on the method it might be

constrained to actually stay in this state, which for a given temperature  $\ensuremath{\mathbb{T}}$  and  $k_B=1$  is defined as

$$\rho_{\rm B}^{\beta} = \mathcal{Z}^{-1} e^{-\beta H_{\rm B}} \quad \text{with} \quad \mathcal{Z} = \operatorname{tr} \left\{ e^{-\beta H_{\rm B}} \right\}, \beta = \mathcal{T}^{-1}.$$
(2.6)

Due to its simple form and the resulting vanishing of  $[\rho_B^\beta, H_B]$ , various computations become easier for this initial state and we are able to reach more concrete results than for an arbitrary bath state.

## THE ENVIRONMENT AND ITS DESCRIPTION

All theoretical investigations of physical systems inherently make a transition from some inspiring original system to the actual mathematical description. The former oftentimes is desired to be a realistic configuration, observable in nature or experiments and incorporating physical phenomena of interest, but in modern physics it is well-established to work with toy models or hypothetic systems as well. This relaxation of requiring "relevance to the real world" leads to several questions for our work, as it includes the transition from an arbitrary - and in particular an arbitrarily big - system to a finite-sized approximation, requiring us to find computationally efficient implementations of the most important features found in the original system. Some central questions we encounter are:

*By which means can the approximation via a finite system be rated? What makes it a good model to represent its mother system?* 

Which properties of the original system are considered to be fixed, i. e. what is the true starting point of investigation? Is the description based on measurements or theory?

When enforcing the connection of a research project with the real world, some of these questions can be answered rather strictly, excluding purely hypothetic systems and proclaiming experimental knowledge to be the final authority. However, investigations not restricted to a specific system but to a generalized class of systems, which thus are dealing with more abstract and theoretical representations, come with the need to answer the above questions. In this chapter, we will address exactly this challenge as well as our way of rating different approximations to the system which we want to describe.

We introduced our system in chapter 2 as a small finite system, the OQS in interaction with an infinite collection of bath modes. This description is motivated by theory and basically results from extending the same system with a finite bath in the thermodynamic limit; As we will see below, there is the need for a constraint on the *total coupling* when performing this limit in order to arrive at a correct discrete representation of the continuous bath.

Hypothetically, one now could treat the system as dependent on the infinite set of parameters  $\{(\Omega_k, \tilde{g}_k)_k \text{ and therefore remain in a very general setting. However, this would be fairly unreasonable as practicality and utility are lost: The former becomes apparent when we try to implement the system numerically, confronting us with the need to truncate the bath in general, but also requiring us to set every$ 

single coupling parameter to a value which is a priori not constrained. This requirement introduces inconvenient effort when setting up the system. The latter problem is clear by the fact that the system's behaviour will depend on the specific values of the bath parameters, preventing us from analyzing the system in the generalized setting but introducing a dependency on the combination of the  $\tilde{g}_k$ . Although the influence of the bath - and therefore of the coupling parameters - on the OQS can be shown to be restricted to second order fluctuations of the bath coupling operators, i. e. to the correlation functions [1, 14], we require a proper procedure for choosing the single couplings in order to usefully pick the systems we want to simulate and gain insights on the behaviour of the general system. The spectral density  $\mathcal{J}$  will allow for a systematic choice of the couplings and its accurate reproduction with a discretized system will be of major importance, as the entire bath influence is traced back to the density via (c. f. section 3.1)

$$c(\tau) = \int_0^\infty d\omega \ \mathcal{J}(\omega) \left[ \cosh\left(\frac{\beta\omega}{2}\right) \cos(\omega\tau) - i\sin(\omega\tau) \right].$$
(3.1)

Having evaluated the need for constraints on the bath parameters, we therefore want to perform the following two steps towards a manageable yet useful system description:

**1.** We introduce the spectral density  $\mathcal{J}$  of the bosonic bath and demonstrate its relations to our system in the thermodynamic limit, to other common bath properties and, most importantly, to experiments. From our starting point 2.5 we can introduce  $\mathcal{J}$  in a rather pragmatic way via

$$\mathcal{J}(\omega) = \sum_{k=1}^{\infty} \tilde{g}_k^2 \, \delta(\omega - \Omega_k) \tag{3.2}$$

which guarantees consistency with the replacement

$$\sum_{k=1}^{\infty} \tilde{g}_k^2 f(\Omega_k) \to \int_0^\infty d\omega \, \mathcal{J}(\omega) f(\omega). \tag{3.3}$$

So far, we did not gain much, because  $\mathcal{J}$  just summarizes the parameters of the bath, but it is the connection of  $\mathcal{J}$  to other theories of systems like our environment and to real world measurements that makes this replacement valuable.

The spectral density is related to the Density Of States (DOS) of the bath in an obvious fashion when expressing the latter as  $D(\omega) = \sum_{k=1}^{\infty} \delta(\omega - \Omega_k)$ , showing its meaning explicitly: In order to determine the number of states N<sub>I</sub> in a given frequency interval I = [a, b], one simply integrates the DOS and receives

$$N_{I} = \int_{a}^{b} d\omega D(\omega) = |\{\Omega_{k} | a \leq \Omega_{k} \leq b\}|.$$
(3.4)

As the DOS is a central quantity in condensed matter physics, being derived in models of various systems and measured (indirectly) in experiments, this connection between  $\mathcal{J}$  and D is valuable for our description.

Hence, the spectral density can be obtained from measurements on physical systems and thus immediately allows for the consideration of realistic systems. This is a big advantage over purely hypothetic setups because the entire behaviour of the physical system is captured and complicated phenomena of the bath dynamics are respected automatically rather than having to be implemented based on a theory. Obviously, this is not helpful in order to *understand* the underlying concepts that lead to the spectral density but provides us with a method in accordance with the open quantum system approach, dealing with the bath only as detailed as necessary and using the spectral density as single input parameter.

An example of the above could be the setting of a single molecule as it is represented in our spin-boson model 2.6. A naive approach would consider a discrete set of transition frequencies for the vibrational degrees of freedom, modelling them as harmonic subsystems. The discreteness would be due to the finite number of atoms in the molecule and the subsequently finite number of DOFs found in the vibrations. However, a realistic system will exhibit a much richer spectrum, based on thermal broadening of the characteristic peaks, complex dynamical interplay between mechanic and electronic properties of the molecule, solvent influences and more [12, 13, 32]

It therefore seems a hopeless endeavour to control a real-world setup sufficiently, e. g. by cooling it down close to absolute 0, for these effects to vanish. On the other hand, realizing a theory that takes into account all aspects that influence the spectrum of the environment poses a huge challenge, which will change with the considered system and requires experimental validation on its own. Consequently, working with  $\mathcal{J}$  as only quantity which mediates bath influence on the OQS is reasonable while allowing for the construction of a manageable model. The input for the spectral density in turn can come from experiment or theoretical models because the connection to both, measured quantities and theoretical parameters, is well-established.

As mentioned earlier, we want to emphasize a constraint on the spectral density - or on the couplings  $\tilde{g}_k$  when understanding  $\mathcal{J}$  as given input - which readily results from 3.2 via integration:

$$\sum_{k=1}^{\infty} \tilde{g}_k^2 = \int_0^{\infty} d\omega \,\mathcal{J}(\omega) \tag{3.5}$$

This condition will play a central role in the following second step towards the discretized model (also c. f. section 3.2).

2. Having introduced the spectral density, we are facing the challenge

of converting the now truly infinite system into a model which can be handled numerically but manages to describe the key features of the bath effects on the open system well. This conversion will be referred to as *bath discretization* and has been a topic of research on its own in the last decades [26, 42, 43, 47, 48]. While we here want to emphasize the conceptual aspect of discretization, we will summarize parts of this research following [42] and elaborate on the resulting methods including their numerical implementations in section 3.2.

As it was emphasized before, the transition to the continuous description is a necessary step in order to incorporate a realistic system in our theoretical description. However, the goal to explicitly compute system dynamics and properties not only analytically but also numerically requires us to restrict ourselves to finitely many bath modes while trying to mimic the original system as good as possible. We will use the correlation function to test such a restriction, using the wellrecognisable phenomenon of correlation revivals in finite systems. It should be emphasized that the idea is not to generate a perfect description of the correlation function while making the bath finite, but that only for a restricted timescale the behaviour of the bath is well-modeled by its finite approximation. This scale can be interpreted as the time that excitations need to "flow through the bath and back" to the system we are observing and it is clear in this (intuitive) picture, that increased bath sizes will increase this time. For linear bath discretization, this expectation can be validated via Fourier analysis and for other discretization schemes we will confirm it in section 3.2

#### 3.1 BATH CORRELATION FUNCTIONS

Before turning to the investigation of various bath discretization techniques, we introduce the bath correlation function(s) which will be involved in rating these methods.

In previous works, it has been stated that the entire influence of the bath on an OQS is encoded in the correlation function which clearifies the importance of this quantity and its proper computation, for example in numerical simulations of a system [42]. This statement, clearly being true within the framework of Master Equations (c. f. chapter 4), is not obvious when treating the entire system dynamics incorporating the bath explicitly. However, one can extract this insight by analyzing the OQS dynamics with mathematical rigour. In [14], the investigation of OQSs interacting with a linear bath like ours shows that the influence of the latter is reduced to second order correlations and in [1] N-time correlations are shown to depend on N + 1-time correlations of the bath. Thus the correlation function is the central quantity with which we can observe the approximative behaviour of a discretized bath

towards its continuous (i.e. infinite) counterpart. We start by defining the correlators<sup>1</sup>

$$\begin{array}{lll} \alpha^+(t,\tau) &=& tr \left\{ V_t B^\dagger \, V_{t-\tau} B \, \rho_B^\beta \right\} \\ \alpha^-(t,\tau) &=& tr \left\{ V_t B \, V_{t-\tau} B^\dagger \, \rho_B^\beta \right\} \end{array}$$

and observing that they do not depend on the time t but only on the time difference  $\tau$  because of the thermal bath state, which commutes with the bath time evolution operator, inviting us to simply write  $\alpha^{\pm}(\tau) = \alpha^{\pm}(t + \tau, \tau)$ . We next turn to our system and determine the more explicit form these functions take when plugging in B<sup>†</sup> and B, which requires us to compute

$$\begin{split} tr \left\{ V_{\tau} B^{\dagger} \ B \rho_{B}^{\beta} \right\} &= \sum_{\{n_{l}\} \in \mathbf{N}_{0}^{\infty}} \langle \{n_{l}\} | V_{\tau} B^{\dagger} \ B \rho_{B}^{\beta} | \{n_{l}\} \rangle \\ &= \sum_{\{n_{l}\} \in \mathbf{N}_{0}^{\infty}} e^{i\tau E} \langle \{n_{l}\} | B^{\dagger} e^{-i\tau H_{B}} B | \{n_{l}\} \rangle e^{-\beta E} \mathcal{Z}^{-1} \\ &= \sum_{\{n_{l}\} \in \mathbf{N}_{0}^{\infty}} \sum_{k,m=1}^{\infty} e^{i\tau E} \tilde{g}_{k} \tilde{g}_{m} e^{-i\tau (E-\Omega_{m})} e^{-\beta E} \mathcal{Z}^{-1} \\ &\times \sqrt{n_{k}} \sqrt{n_{m}} \langle \{n_{l}, n_{k} - 1\} | \{n_{l}, n_{m} - 1\} \rangle \\ &= \sum_{k=1}^{\infty} \tilde{g}_{k}^{2} e^{i\tau \Omega_{k}} \sum_{\{n_{l}\} \in \mathbf{N}_{0}^{\infty}} n_{k} e^{-\beta E} \mathcal{Z}^{-1} \\ &= \sum_{k=1}^{\infty} \tilde{g}_{k}^{2} e^{i\tau \Omega_{k}} \langle n_{k} \rangle_{\beta} \\ tr \left\{ V_{\tau} B \ B^{\dagger} \rho_{B}^{\beta} \right\} &= \sum_{k=1}^{\infty} \tilde{g}_{k}^{2} e^{-i\tau \Omega_{k}} \left( \langle n_{k} \rangle_{\beta} + 1 \right). \end{split}$$

Here,  $|\{n_l\}\rangle$  denotes a Fock basis state, which also is understood as occupation number basis,  $\mathcal{Z}$  is the partition sum of the thermal state (c. f. 2.6) and for notational convenience we wrote  $|n_1, n_2, ... n_k - 1, ...\rangle$  as  $|\{n_l, n_k - 1\}\rangle$  and abbreviated the energy of the state  $|\{n_l\}\rangle$  as E, suppressing its dependence on the occupation numbers. However, this abuse of notation is restricted to the above computation. For the bosonic system under consideration we know the thermal expectation value of the single-site occupation number to be given by the *Bose-Einstein distribution* 

$$\langle \mathbf{n}_k \rangle_\beta = \mathbf{n}(\Omega_k) = (e^{\beta \Omega_k} - 1)^{-1}$$
 (3.6)

which allows for a convenient extension to the present case of infinitely many bath modes in the continuous description. This becomes apparent in the next step when employing the replacement 3.3 in

<sup>1</sup> For notation see chapter 2.

the correlators. We additionally turn to the sum of both functions instead of treating them separately, as they will only contribute in this summed form throughout our work. The resulting function will be referred to as *correlation function* and denoted by c:

$$c(\tau) = \int_{0}^{\infty} d\omega \, \mathcal{J}(\omega) \left[ e^{-i\tau\omega} n(\omega) + e^{i\tau\omega} (n(\omega) + 1) \right] \quad (3.7)$$
$$= \int_{0}^{\infty} d\omega \, \mathcal{J}(\omega) \left[ \cos(\tau\omega) (2n(\omega) + 1) - i\sin(\tau\omega) \right]$$

As discussed earlier, the correlation function is seen as central quanitity encoding the bath influence on the open system in OQS theory although there is no obvious proof for this in other frameworks; Still, the importance of c remains without doubt. Its decay behaviour is used to determine whether the Markov approximation is justified and for master equations it indeed contains all information of the bath considered in the time evolution of the OQS. Therefore, using the correlation function to test approximation schemes for the bath is the obvious choice and we will focus on the phenomenon of revivals and the corresponding revival time when doing so below.

#### 3.2 BATH DISCRETIZATION

In this section we want to turn to the concrete techniques which can be used in order to transit from the continuous bath description to a finite approximative model, following [42] which is recommended as a review of the subject. Additionally, we will explore the parameter space for our system with respect to the different methods and numerically evaluate their differences.

The discretization of the bath aims at generating a finite set of parameters  $\{(\Omega_k, \tilde{g}_k)\}_{1 \le k \le L}$  for L bath modes.<sup>2</sup> When doing so, a single constraint is to be considered, which can be referred to as normalization condition and was introduced earlier in 3.5:

$$\sum_{k=1}^{L} \tilde{g}_{k}^{2} = \int_{0}^{\infty} d\omega \,\mathcal{J}(\omega)$$
(3.8)

After looking at the spectral densities we are going to consider (c. f. appendix A), we actually replace the upper integration boundary by  $\omega_{cut}$  exploiting the step cutoff contained in all examples for  $\mathcal{J}$ . If it was not before, it is now obvious that the normalization constraint resembles a quadrature.

<sup>2</sup> Please note that we do not distinguish the notation between the original infinite set of parameters and the result of the discretization. This is not critical as they never play a role at the same time and the infinite set is never used concretely.

#### Discretization Schemes

The first, obvious attempt of discretization is to perform the quadrature via a Riemann sum. This is done by generating the  $\{\Omega_k\}$  as an evenly spaced set with spacing distance  $\delta \omega$  and assigning values to the  $\tilde{g}_k$  by evaluating  $\mathcal{J}$  at those frequencies:

LINEAR SAMPLING 
$$\begin{array}{rcl} \Omega_{k} &=& k \cdot \delta \omega - \frac{\delta \omega}{2} & \text{with} & \delta \omega = \frac{\omega_{\text{cut}}}{L} \\ \tilde{g}_{k} &=& \sqrt{\delta \omega \, \mathcal{J}(\Omega_{k})} \end{array}$$
 (3.9)

For large L, the approximation is improved and the limit  $L \rightarrow \infty$  actually corresponds to the integral itself by definition as  $\delta \omega \rightarrow d\omega$ . Due to its simplicity, this sampling is commonly used [33].

On the pursuit of improving the approximation, the first step is to generalize the intervals  $I_k$  into which the support of  $\mathcal{J}$  is separated and to compute the couplings as integral and the frequencies as weighted average over these intervals, respectively. This yields a rather general rule for discretization which relies on an adequate choice of the  $\{I_k\}_k$ . This choice in turn will depend on the methods used on the discretized system, the properties of the spectral density and also on the phenomena one is interested in, such as the behaviour for specific energy scales. Commonly used samplings in addition to the linear spacing include logarithmic [11, 17, 38] and cosine spacings [45] as well as piecewise combinations of those [44].

We summarize this generalized quadrature rule as

Direct Sampling  

$$\tilde{g}_{k} = \sqrt{\int_{I_{k}} d\omega \, \mathcal{J}(\omega)} \quad (3.10)$$

$$\Omega_{k} = \tilde{g}_{k}^{-2} \int_{I_{k}} d\omega \, \omega \mathcal{J}(\omega)$$

where the name refers to the fact that we previously fixed the intervals  $\{I_k\}_k$  and this choice dictates the sampling outcome.<sup>3</sup> Note that the quadrature is perfect in this case, as the sum over the squared couplings is just a concatenation of the partial integrals over the respective interval.

The direct sampling introduces k - 1 degrees of freedom corresponding to the k + 1 endpoints of the intervals except for 0 and  $\omega_{cut}$ , which reminds us of the initial situation we wanted to avoid by introducing the spectral density of the bath (c. f. chapter 3). Although being a possibly mighty tuning parameter to adapt the discretization to a specific problem [43, 50] or to prevent certain numerical methods from failing (such as numerical renormalization group), this huge flexibility is a possible source for bias and like the problematic situation introduced by 2k freely chosen parameters for the bath, a major dependence on

<sup>3</sup> In [42], the name direct sampling refers to all classic sampling methods, including the linear as well as the mean and equal-weight sampling methods.

the free choice of interval separation makes the direct discretization method unfavourable to us.

Instead, we want to briefly recap two sampling strategies proposed in [42] before turning to the so-called optimized sampling procedure. The first is called mean method and constructs the bath mode frequencies iteratively by averaging over stepwise refined intervals. This gives a single frequency  $\Omega_1$  in the first step and  $2^p - 1$  sampled frequencies after p steps. Once we reach the desired fine-graining, we relabel the frequencies in ascending order and the couplings are computed as integrals over the resulting intervals:

$$\Omega_{k} = \left( \int_{\Omega_{k-1}}^{\Omega_{k+1}} d\omega \, \mathcal{J}(\omega) \right)^{-1} \int_{\Omega_{k-1}}^{\Omega_{k+1}} d\omega \, \omega \mathcal{J}(\omega)$$
Mean Sampling
$$\tilde{g}_{k}^{2} = \int_{\frac{\Omega_{k-1}+\Omega_{k}}{2}}^{\frac{\Omega_{k+1}+\Omega_{k}}{2}} d\omega \, \mathcal{J}(\omega) \qquad (3.11)$$

where the first line only holds for the frequencies which are added in the last step. Note that for this procedure no choice of intervals had to be made but that as a drawback this sampling only allows for  $L \in \{2^p - 1 | p \in \mathbb{N}\}$  in a consistent spacing.

This limitation is overcome by yet another discretization technique, for which one starts with computing the "coupling per mode" n for a given L. Afterwards the intervals for the discretization are obtained by demanding the contribution of each mode to be equal to n and the frequencies are set to the average over these intervals as before:

$$n = \frac{1}{L} \int_{0}^{\omega_{cut}} d\omega \,\mathcal{J}(\omega)$$
EQUAL-WEIGHT
$$g_{k}^{2} = n \text{ and } \int_{\omega_{k-1}}^{\Omega_{k}} d\omega \,\mathcal{J}(\omega) \stackrel{!}{=} n \qquad (3.12)$$

$$\Omega_{k} = \left( \int_{\omega_{k-1}}^{\omega_{k}} d\omega \,\mathcal{J}(\omega) \right)^{-1} \int_{\omega_{k-1}}^{\omega_{k}} d\omega \,\omega \mathcal{J}(\omega)$$

With this method, we are able to capture specifics of the spectral density such as peaks, which will cause the algorithm to sample more densely, and no parameters have to be chosen.

So far, all discretization techniques do either ignore the different energy scales by treating the spectrum "uniformly" or choose a specific scale at which the discretization is supposed to work best, e.g. logarithmic sampling focuses on low energy scales. As the energy scales correspond to timescales in the correlation function and therefore in the system dynamics, it is desirable to achieve discretization which is suitable at all scales in order to describe short- and long-time evolution correctly.

The main algorithm treated in [42] and referred to as *optimized sampling*, tries to accomplish this goal and we will discuss it in the following

by looking at the derivation, the numerical implementation, which is universal w.r.t.  $\mathcal{J}$ , and by evaluating in which cases the optimized sampling actually is an improvement.

The new sampling method uses *Gaussian quadrature*, which is a far developed topic because of its age and wide range of applications, additionally coming with well-established numerical methods. In order to employ the quadrature rule, we need to introduce the concept of orthogonal polynomials, which is done in appendix B. The key features we are going to use here are the existence of a unique set of such polynomials for a given continuous measure and the recursion relation which generates them.

The Gaussian quadrature rule proceeds as follows: Let us consider the integral we want to approximate,  $\int_0^{\omega_{cut}} d\omega \mathcal{J}(\omega)$ , and split up the integrand  $\mathcal{J}(\omega)$  into a part which is considered as weight function  $w(\omega)$  and its complementary part  $u(\omega)$ . As the weight function gives rise to a continuous measure, different choices of w lead to different orthogonal polynomials in the following procedure and investigations of dynamical error bounds on the time evolution of discretized systems suggest that these choices actually are of different quality [47, 48]. In the following, we will assume  $w(\omega) \ge 0$ , a finite support and continuity of w.

After chosing L points  $\{\omega_i\}_i$  in the support of *w*, we can construct polynomials

$$\ell_{i}(\omega) = \prod_{k \neq i} \frac{\omega - \Omega_{k}}{\omega_{i} - \Omega_{k}}$$
(3.13)

of degree L – 1 which satisfy  $\ell_i(\omega_j) = \delta_{ij}$ . Then we look at the function u and again split it into two parts, an interpoland  $u_L$  of degree L – 1 and the residual part  $r_L$ . Constraining  $u_L$  to coincide with u at the above L points, it is uniquely determined and we can easily expand it in the polynomials via

$$u_{L}(\omega) = \sum_{i=1}^{L} u(\omega_{i})\ell_{i}(\omega).$$
(3.14)

The integral from above now reads

$$\int_{0}^{\omega_{cut}} d\omega \mathcal{J}(\omega) = \int_{0}^{\omega_{cut}} d\omega w(\omega) \left[ \sum_{i=1}^{L} u(\omega_{i})\ell_{i}(\omega) + r_{L}(\omega) \right]$$
$$= \sum_{i=1}^{L} W_{i} u(\omega_{i}) + R_{L} \qquad (3.15)$$
with  $W_{i} = \int_{0}^{\omega_{cut}} d\omega w(\omega)\ell_{i}(\omega)$ and  $R_{L} = \int_{0}^{\omega_{cut}} d\omega w(\omega)r_{L}(\omega).$ 

It is obvious that for u with degree up to L - 1 the interpoland  $u_L$  is able to describe the function exactly, yielding  $r_L(\omega) \equiv 0$  and  $R_L = 0$ . As can be shown, the quadrature even is of order 2L - 1 which means it is exact in the integration for deg  $u \leq 2L - 1$ , rendering  $R_L = 0.4$  As one can show, this is achieved by choosing the support points  $\{\omega_i\}_{1 \leq i \leq L}$  to be the roots of the orthogonal polynomial  $p_L$  of degree L [40], where orthogonality is understood w.r.t. *w* as introduced in appendix B. In addition to the sampling points  $\Omega_k$  gained in this fashion, the weights  $W_i$  can be extracted from the system of orthogonal polynomials as we mentioned in appendix B and is shown in [18, 37]. We then simply draw the analogy between the spectral density normalization condition 3.5 and the quadrature 3.15 and identify

$$\begin{array}{c} \text{roots} \ \{\omega_{i}\}_{i} \\ \text{weights} \ \{W_{i}\}_{i} \end{array} \right\} \rightarrow \begin{cases} \text{bath frequencies} \ \{\Omega_{k}\}_{k} \\ \text{bath couplings} \ \{\tilde{g}_{k}^{2}\}_{k} \end{cases}$$
(3.16)

This optimized sampling can be shown to be optimal for quadratic Hamiltonians whereas no optimal solution is enforced by the above strategy for non-quadratic Hamiltonians [42]. We therefore, dealing with the latter case, will have to evaluate the properties of this newer method, where for convenience we will compare to the most simple method namely linear sampling. This investigation is presented in the following.

#### Rating Discretizations

In order to rate the discretization schemes, we first introduce the notion of the revival time  $\tau_{rev}$ , which is defined as the time up to which the correlation function of an environment is well reproduced qualitatively. Although there are recognizable deviations from the approximated correlation function for very small numbers of bath modes before  $\tau_{rev}^{5}$ , the revival time will first be considered as criterion for the minimal bath mode number needed in order to describe the system. Afterwards, the initial deviation  $\sigma$  shall be treated. An example of the revivals occuring for finite environments is displayed in fig. 3.1, where an increase of the bath size L is seen to push the revival time further away from 0. We observe very well coinciding results up to the respective revival time, excluding very small bath approximations as mentioned above, for which already at earlier times  $\tau < \tau_{rev}$  the correlation function is not reproduced properly. In 4.12 the only contribution of the bath is encoded precisely in the correlation function up to the current time, and for a quick decay in  $c(\tau)$ , only the integrated correlation function at infinity is accounted for in 4.14, not being distinguished from the current value  $\kappa(t)$  because of

<sup>4</sup> Note, that this does not imply  $r_L \equiv 0$ , which for deg  $u \ge L$  is wrong.

<sup>5</sup> Especially for linear sampling, c. f. analysis below.

this decay. This demonstrates that for the description of our system with the master equation, a sufficiently big finite system gives us the same results as the infinite original - while being computationally manageable - as we only use well-reproduced quantities.<sup>6</sup> In order to determine the revival time in an automated fashion, we subtract the correlation function of the finite bath from the continuous case and observe this difference to be a simple oscillation, shifted by a constant for some parameter settings. We therefore compute the scale of the deviation, accounting for the oscillations, and calculate the revival time as last maximum of magnitude that is not bigger than this averaged amplitude.

The second way to rate the discretization of the bath is to quantify the deviation of the reproduced correlation function *before*  $\tau_{rev}$ . We will do so by computing

$$\sigma = \sqrt{\tau_{re\nu}^{-1} \int_0^{\tau_{re\nu}} d\tau \, |c_{\infty}(\tau) - c_{\rm L}(\tau)|^2}, \qquad (3.17)$$

which for discretized time steps corresponds to the standard deviation of the correlation function for L modes from the correlation function of the infinite bath denoted by  $c_{\infty}$ . Exemplarily, we can compute this quantity for the discretizations in fig. 3.1 and their linearly sampled counterparts and arrive at

L	8	12	16
$\sigma_{opt}[meV]$	11.2	2.2	1.3
$\sigma_{lin}[meV]$	26.0	17.7	13.4

For optimized sampling, we observe a drastic improvement in the precision at which  $c(\tau)$  is reproduced for  $\tau < \tau_{rev}$  with growing L, whereas the linear bath shows worse values in general, which additionally improve much less for increased bath sizes.

We now can rate discretization schemes by determining the achieved revival time  $\tau_{rev}$  and the corresponding deviation  $\sigma$  for a given bath size L, which in turn is desired to be small in order to render smaller systems. However, it should be noted that a *good* representation of the bath which shows earlier revivals is more important than a mediocre one which lasts longer. We therefore are going to analyze both properties simultaneously putting emphasis on small  $\sigma$  but also taking care of  $\tau_{rev}$  in order to assure a discretization with overall useful properties.<sup>7</sup>

<sup>6</sup> For the Markovian Master Equation (MME), it then obviously is important to simulate  $\kappa(\infty)$  by  $\kappa(T)$  with  $T < \tau_{rev}$  in order to avoid revivals to change  $\kappa(T)$ .

<sup>7</sup> A very precise reproduction of c at the cost of too small  $\tau_{re\nu}$  would not be very helpful for the later simulations.



Figure 3.1: Demonstration of revivals in the optimized sampled finite bath correlation function (exemplarily its real part) for various bath sizes L at typical bath parameters with  $\beta = 10 \text{ eV}^{-1}$ .

For this, we choose a spectral density of Caldeira-Leggett type (see appendix A)

$$\mathcal{J}(\omega) = \alpha \left(\frac{\omega}{\omega_{\rm c}}\right)^{\rm s} e^{-\omega/\omega_{\rm c}}$$
(3.18)

which leaves us with the following parameters<sup>8</sup>:

$$\omega_{\rm c}, \omega_{\rm cut}, s, \beta, L$$
 (3.19)

The choice of these parameters - or more precisely their range - shall be motivated in the following way: We want to investigate the discretization of baths that can be relevant for the main computations in part ii, and inspired by the spectral density of Rhodamine with its group of main peaks located around 0.2 eV (see appendix A) we choose  $\omega_{c} \in [0.2, 0.5]$ ;  $\omega_{cut}$  will in turn be given as a multiple of the critical frequency and we choose  $\omega_{cut}/\omega_c \in [1, 10]$  based on standard choices for this proportion and the fact that contributions with  $\omega \gg \omega_c$  are suppressed exponentially.9 The Ohmicity of the bath, parametrized by s, depends on several parameters of the described system, such as the effective dimension of the phononic bath, and will be chosen from  $\{0.5, 1, 2\}$ . As an example, in addition to the aforementioned peaks the spectrum of Rhodamine contains a smooth background that can be described by an ohmic spectral density that is a density  $\mathcal{J}$  of type 3.18 with s = 1. It is this continuous part that we want to discretize and the peaks, already discrete, are added independently. Finally,  $\beta$  can be adapted to realistic values of the bath temperature T, which range up to room temperature ( $T \approx 300$ K,  $\beta > 40 \text{ eV}^{-1}$ ), and L will be restricted

<sup>8</sup> As for the correlation function we have  $c(\tau) \propto \alpha$ , we fix  $\alpha \equiv 1$  throughout this section.

<sup>9</sup> Standard choices for  $\omega_{cut}/\omega_c$  are 2, 4 and 10 and for the main analysis of this work, we will mostly consider  $\omega_{cut} = 2\omega_c$ .

to [5,50]. It shall be noted that for some toy model computations and demonstrations, such as fig. 3.1, we sometimes choose values outside of these ranges in order to reach computationally convenient parameter regimes.

First of all, we look at the influence of the temperature and the bath



Figure 3.2: Revival time  $\tau_{rev}$  for various bath sizes L and temperatures  $\beta$  at fixed parameters  $\omega_c = 0.3 \text{ eV}$ ,  $\omega_{cut} = 0.6 \text{ eV}$  and s = 1 of the spectral density. The plot on top displays the standard deviation of  $\tau_{rev}$  along vertical lines, i.e. for a constant bath size. The optimized sampling method was used.

size on  $\tau_{re\nu}$ , which is shown in fig. 3.2. It can be seen that the dependence on L is strictly monotonous as expected, in correspondence to the limit  $L \to \infty$  towards the continuous system. In contrast, we do not observe any significant dependence on  $\beta$ , even though we are looking at a properly big parameter range. This can be seen from the absence of any trend within the main plot itself and in more detail from the very small standard deviation  $\varepsilon(\tau_{re\nu})$  displayed in the upper part of fig. 3.2. For linearly sampled baths, the influence of  $\beta$  is even smaller (c. f. fig. D.1 in appendix D). This independence, as we want to emphasize, only regards the revival time and not the details of the correlation function itself, which in general will exhibit temperature dependent behaviour.

After having observed the temperature influence to be fairly small, we turn to the comparison between the linear and the optimized sampling method for various bath sizes. Exemplary results are shown in fig. 3.3, calling our attention to the opposite results compared to our expectation: The linear sampling method actually yields *bigger* 



Figure 3.3: Comparison of the revival time between linear (dashed) and optimized (solid) sampling in dependence of the bath size for the same spectral density as in fig. 3.2 and at two exemplary temperatures. The simulation induces a bound to  $\tau_{rev}$  at 300  $eV^{-1}$  which is to be ignored.

revival times than the optimized method for all evaluated bath sizes;<sup>10</sup> The slope is roughly the same for both methods but a constant offset puts the linear sampling in favor. Please note that the simulational upper boundary in time was chosen to be 300  $eV^{-1}$  such that the computed revival time is bounded by this value as is apparent in the linear sampling case.

In conclusion, as we have encountered a whole parameter regime for which the optimized sampling is not optimal - at least by means of the revival time - we would have to determine which sampling strategy is to be used depending on the parameters for each simulation. But before deciding on this approach, we turn to the second measure of quality for the discretization, that is the averaged deviation of the finite from the infinite bath correlation function  $\sigma$  as introduced in 3.17. It is shown in fig. 3.4 for the same baths as in fig. 3.2 and suggests using the procedure of optimized sampling: The averaged deviations are very small with exceptions for some specific smaller bath sizes. As these exceptions mainly lie on isolated lines for a fixed L, we interpret them to be an issue arising from increased oscillations in the initial deviation. This can be understood as follows: For smaller baths it is possible that the transition between the time frame for which c(t) is reproduced properly and the frame including correlation revivals is rather smooth, similar to the behaviour of polynomial series expansions for low orders. Thus, the revival time detection method becomes less precise and the first increased deviations immediately before the detected revival time are included in the computation of  $\sigma$ . However,

<sup>10</sup> A further analysis in fig. D.2 shows that for the entire parameter range displayed in fig. 3.2 the linear sampling method has bigger revival times as expected from combining the insights of fig. 3.2 and 3.3.



Figure 3.4: Deviation  $\sigma$  for the same parameters as in fig. 3.2. The optimized sampling method was used.

we were not able to find any systematic problem with the computation and claim the seen structures to be not physical but numerical artefacts. It should be noted, that even for the increased  $\sigma$ , we observe a very small deviation for the optimized sampling overall. In contrast, the linear sampling method generates much bigger deviations as is shown in fig. 3.5<sup>11</sup> and can be read off immediately of fig. D.3. We want to note that observing an improved revival time in the linearly compared to the optimized sampled bath does not contradict the optimality statement in [42] because the revival time is not the main criterion for optimality in the sense of properly reproduced OQS dynamics. As argued before, obtaining well-reproduced correlations for  $\tau < \tau_{rev}$  is more important that increasing  $\tau_{rev}$  alone. Additionally, it should be noted that improvements via linear sampling regarding the revival time lie in the range of several %, whereas the averaged deviation  $\sigma$ is reduced by at least one, typically even by two orders of magnitude when switching to optimized sampling. For future works it would be interesting to investigate the relation between the Markovianity of the bath and the deviation  $\sigma$  as well as the revival time  $\tau_{rev}$ .

Next, we consider the influence of the spectral density parameters  $\omega_c$  and  $\omega_{cut}$  on the revival and precision of  $c(\tau)$ . In fig. 3.6 a corresponding set of typical parameters is investigated, clearly displaying a revival time dependence on the two parameters. We observe slightly differing revival times for the two sampling methods and a comparison shows that typically for  $\omega_{cut}/\omega_c \ge 6$ , the optimized sampling

<sup>11</sup> Please note the different colour scales between fig. 3.4 and 3.5.



Figure 3.5: Deviation  $\sigma$  for the same parameters as in fig. 3.2. Here the linear sampling method was used.



Figure 3.6: Dependence of  $\tau_{rev}$  on the spectral parameters  $\omega_c$  and  $\omega_{cut}$  for fixed bath size L = 20, ohmicity s = 1 and inverse temperature  $\beta = 100 \text{ eV}^{-1}$ ; (a) Optimized sampling, (b) Linear sampling.

yields bigger  $\tau_{rev}$  whereas in the range  $\omega_{cut}/\omega_c \leq 3$  the linear sampling has increased revival times. However, we again want to consider the quality of the reproduced correlation function and for this take a look at  $\sigma$  depending on  $\omega_c$  and  $\omega_{cut}$ . The result is shown in fig. 3.7 again for both methods, leaving us with deviations on two very different scales.<sup>12</sup> Given the fact that the smallest deviations in the linearly sampled bath occur for settings which produce the biggest  $\sigma$  in the optimized sampling, we actually can observe cases for which  $\sigma_{lin} < \sigma_{opt}$  but it should be noted that these are corner cases for very big  $\omega_{cut}/\omega_c$ . Away from this special regime, the linear sampling

<sup>12</sup> The computation of  $\sigma$  becomes less reliable for small  $\tau_{rev}$ , which can be observed in the optimized sampling setting for big  $\omega_{cut}$ . Again we claim the irregular results for  $\sigma$  to be of numerical origin.

reproduces  $c(\tau)$  much worse than the optimized technique, which becomes apparent from the scales in fig. 3.7.

In summary, we were able to observe improved reproduction of the





(a) Optimized sampling, (b) Linear sampling.

continuous correlation function by the optimized sampled discrete bath. The few corner cases we found to deviate from this general statement show that this is not a strict rule but for the parameter regimes we are interested in, it is reasonable to state:

The optimized sampling method generates a bath which reproduces the correlation function - and therefore the entire influence of the bath on the OQS better than the linear sampling method for times  $\tau < \tau_{rev}$ . Even though the revival time itself typically is smaller, the averaged reproduction precision  $\sigma$ is significantly better, in various realistic cases by orders of magnitude.

We therefore will continue to use the optimized sampling technique throughout the upcoming simulations.

### 3.3 TRUNCATION OF THE HARMONIC BATH

As it will be of importance for the numerical implementation of the bath, we want to deal with the topic of truncation of the bath modes in this section. Due to the full realization of each (discrete) bath mode within the DMRG model, we need to replace the bosonic sites of infinite matrix dimension with a finite-dimensional substitution. To this end, we truncate the harmonic modes to a dimension  $m_{bath}$ , which has to be chosen in a trade-off between computational effort and preservation of the physical bath properties.

For the thermal initial state of the bath, we can introduce a condition

on  $m_{bath}$  via the maximal population r of the i-th bath mode that is to be discarded<sup>13</sup>:

$$\mathcal{Z}_{i}e^{-\beta\Omega_{i}\mathfrak{m}_{bath}} \stackrel{!}{\leq} r \quad \Rightarrow \quad \mathfrak{m}_{bath}(\Omega_{i}) < -\frac{\ln r - \ln \mathcal{Z}_{i}}{\beta\Omega_{i}} \qquad (3.20)$$

with  $\mathcal{Z}$  being the partition sum of the untruncated i-th mode. Obviously, the highest dimension is required for the first bath mode with the lowest energy and therefore, regarding  $\rho_B^\beta$  alone, the choice  $m_{bath}(\Omega_1)$  is reasonable.

Another way to choose the truncation relies on the fact that the corre-



Figure 3.8: Maximal deviations of the truncated bath correlation function from the untruncated case for different bath temperatures and truncation dimensions with parameters in 3.21. The error for high temperatures is hard to be reduced to the order of smaller temperatures by increasing m<sub>bath</sub>.

lation function of the bath contains the entire bath influence on the dynamics. Following this train of thought, we can compute  $c(\tau; m_{bath})$  analytically for different truncations and demand convergence in that parameter towards  $c(\tau) = c(\tau; \infty)$ . This could potentially discard significant bath dynamics but due to the above statement will not change the OQS dynamics, which are of our interest after all. Fig. 3.8 shows maximal deviations  $\Delta_{max} = \max_{\tau} \{|c(\tau; m_{bath}) - c(\tau)|/c(0)\}$  of the correlation function from the untruncated case for a discretized bath with<sup>14</sup>

$$L = 100, wc = 0.3, w_{cut} = 0.6, s = 1$$
 (3.21)

and for various inverse temperatures  $\beta$  and bath truncations  $m_{bath}$ . As expected, we see a strong dependence of the difference on the

<sup>13</sup> Please note that there is a correction due to the normalization via the partition sum 2. This influence is small for bath truncation dimensions close to convergence and is neglected here for clarity of the qualitative argument.

<sup>14</sup> As we found the revival time to be independent from  $\beta$ , we choose the same bath size L for all temperatures.
temperature and for high temperatures even very high truncation dimensions do not yield properly small errors. We therefore will have to choose simulational parameters in a reasonable fashion and for cases with high temperatures, the shown uncertainty has to be respected and accounted for when interpreting the results.

In addition to the thermal state analysis we want to consider the following: Due to the interaction with the OQS, we expect populations to be changed throughout the time evolution and depending on the initial conditions, increased populations for some of the bath modes are possible. This is called *bath filling effect* and its role in the DMRG simulation has to be contrasted with the statement above, denying such dynamical influence on the time evolution of the OQS.

However, combining the above ideas and results, we decide the following: For suitable temperatures<sup>15</sup> the deviation of the truncated correlation function is properly small for  $m_{bath} \ge 30$ . Furthermore the maximal discarded thermal population is given for a realistic bath size L = 20, this truncation  $m_{bath} = 30$  and highest temperature  $\beta = 40 \text{ eV}^{-1}$  by

$$r = \mathcal{Z}_{1}^{-1} e^{-\beta \Omega_{1} m_{bath}} = 5.8 \cdot 10^{-4}.$$
 (3.22)

Regarding the bath filling effect, no obvious strict statement can be made but we will have to check on individual cases whether the OQS significantly increases the bath populations, for example by introducing a large amount of energy into the mode closest to resonance with the OQS.

We thus claim  $m_{bath} = 30$  to be a reasonable standard choice of the truncation parameter and will use it unless there is specific reasons to increase it.

<sup>15</sup> The reader shall be reminded that  $\beta = 40$  roughly corresponds to room temperature and therefore smaller  $\beta$  are rather unrealistic for an experiment in the field.

In this chapter we want to derive the ME we use in this work and discuss the approximations considered in the derivation. As is commonly done, we aim at the weak-coupling regime.

For the derivation, we mostly follow [10], chapter II.3.3, but further discussion and elaboration on the details will be added. Starting from the density matrix in the Schrödinger picture  $\rho^{(s)}(t)$  and its time evolution, the interaction picture density matrix  $\rho(t)$  is defined using the interaction-free time evolution operator  $U_0(t)$ ,

$$\rho^{(s)}(t) = U(t)\rho^{(s)}(0)U^{\dagger}(t) \quad ; \quad \rho(t) = U_0^{\dagger}(t)\rho^{(s)}(t)U_0(t), \quad (4.1)$$

and its equation of motion can be computed as

$$\dot{\rho}(t) = \frac{d}{dt}\rho(t) = i[H_0, \rho(t)] - i[V_t H, \rho(t)] = -i[V_t H_I, \rho(t)]$$
(4.2)

which is the von Neumann equation in the interaction picture. Integrating and then iterating this equation gives

$$\rho(t) = \rho(0) - i \int_{0}^{t} d\tau \left[ V_{\tau} H_{I}, \rho(0) - i \int_{0}^{\tau} ds \left[ V_{s} H_{I}, \rho(s) \right] \right]$$
(4.3)

where the starting time was fixed to  $t_0 = 0$  for convenience. By taking the time derivative and tracing out the bath afterwards, the relation becomes

$$\dot{\rho_{S}}(t) = -i \operatorname{tr}_{B} \left\{ \left[ V_{t} H_{I}, \rho(0) \right] \right\} - \int_{0}^{t} ds \operatorname{tr}_{B} \left\{ \left[ V_{t} H_{I}, \left[ V_{s} H_{I}, \rho(s) \right] \right] \right\}.$$
(4.4)

Next, we use the assumption of the initial state being in a product form i.e.  $\rho(0) = \rho_S(0) \otimes \rho_B^\beta$ , as well as the specific linear form of the system-bath coupling, allowing us to compute

$$\begin{aligned} \operatorname{tr}_{B}\left\{\left[V_{t}H_{I},\rho(0)\right]\right\} &= \left[e^{\operatorname{it}H_{S}}\mathcal{A} e^{-\operatorname{it}H_{S}},\rho_{S}(0)\right]\operatorname{tr}\left\{e^{\operatorname{it}H_{B}}\mathcal{B} e^{-\operatorname{it}H_{B}}\rho_{B}^{\beta}\right\} \\ &+ \rho_{S}(0)e^{\operatorname{it}H_{S}}\mathcal{A} e^{-\operatorname{it}H_{S}}\operatorname{tr}\left\{\left[e^{\operatorname{it}H_{B}}\mathcal{B} e^{-\operatorname{it}H_{B}},\rho_{B}^{\beta}\right]\right\} \\ &= \left[e^{\operatorname{it}H_{S}}\mathcal{A} e^{-\operatorname{it}H_{S}},\rho_{S}(0)\right]\operatorname{tr}\left\{\mathcal{B} \rho_{B}^{\beta}\right\} = 0, \end{aligned} (4.5)$$

where the traced term in the last expression is the thermal expectation value of the coupling operator, which can be computed for any integer power  $r \ge 1$  using the occupation number or Fock basis for the single bosonic bath sites:

$$\langle b_{\mathfrak{m}}^{r} \rangle_{\beta} = \sum_{\{\mathfrak{n}_{l}\} \in \mathbf{N}_{0}^{\infty}} \langle \{\mathfrak{n}_{k}\} | b_{\mathfrak{m}}^{r} e^{-\beta H_{B}} | \{\mathfrak{n}_{k}\} \rangle$$

$$= \sum_{\{\mathfrak{n}_{l}\} \in \mathbf{N}_{0}^{\infty}} \left( e^{-\beta \Omega_{\mathfrak{m}} \mathfrak{n}_{\mathfrak{m}}} \underbrace{\langle \mathfrak{n}_{\mathfrak{m}} | b_{\mathfrak{m}}^{r} | \mathfrak{n}_{\mathfrak{m}} \rangle}_{0} \prod_{l \neq \mathfrak{m}} \langle \mathfrak{n}_{l} | e^{-\beta H_{l}} | \mathfrak{n}_{l} \rangle \right) = 0,$$

$$(4.6)$$

Our time evolution equation therefore takes the form

$$\dot{\rho_{S}}(t) = -\int_{0}^{t} ds \ tr_{B} \left\{ \left[ V_{t} H_{I}, \left[ V_{s} H_{I}, \rho(s) \right] \right] \right\}$$
(4.7)

which is exact so far, given the thermal initial bath state and a coupling between the bath and the system which is linear in the bath operators.

#### 4.1 BORN APPROXIMATION - WEAK COUPLING

In addition to the assumption  $\rho(0) = \rho_S(0) \otimes \rho_B^{\beta}$  we now perform the Born approximation stating that  $\rho(s) = \rho_{S}(s) \otimes \rho_{B}(0) + O(\alpha^{2})$  holds for all times s, where we introduced the overall scale of the couplings  $\tilde{g}_k$  abstractly called  $\alpha$ .<sup>1</sup> Assuming this scale to be small and understanding that  $H_{I} \propto \alpha$ , we are allowed to replace  $\rho(s) = \rho_{S}(s) \otimes \rho_{B}(0)$ in the r.h.s. of the master equation, in order to gain a consistent perturbative description including second order (in  $\alpha$ ) changes of  $\rho_S$ . The weak-coupling assumption severely restricts the range of applicability of the resulting equation, as it does not consider bath changes above second order consistently and therefore neglects the detailed behaviour of the environment in the case where interactions are strong and higher order correlations may play a relevant role. Also, it prevents entanglement between the bath and the system as can clearly be seen from the product structure of  $\rho$ . The reason why we still invoke the above replacement is simply to arrive at a system description that is handleable both, analytically and numerically, and because weakly coupled systems pose interesting problems to investigate and not only hypothetic toy models.

As one might notice, applying the Born approximation without any further constraints, the description via the master equation *violates energy conservation* as soon as the open system transfers excitations to the bath, which in turn does not leave its thermal state, i. e. as soon as a non-thermal initial state for the combined system of OQS and environment is chosen. For a generalization of the Born approximation which respects energy conservation on its own by allowing for a flexible bath temperature, see [51].

As we shall see below, the Born approximation can be shown to yield reasonable results afterall, including energy conservation, when employed in synergy with other approximation schemes.

We now want to continue with the derivation of the weak-coupling ME: Provided small  $\alpha$ , we can not only invoke the Born approximation, but also replace

$$\rho_{\rm S}(s) \to \rho_{\rm S}(t) + \mathcal{O}\left(\alpha^2\right)$$
(4.8)

<sup>1</sup> For a more precise notion of the coupling strength scale and how the correspondence between the single couplings {g<sub>k</sub>}<sub>k</sub> and the scale α is drawn, see appendix A and chapter 3, in particular section 3.2.

on the r.h.s. of 4.7 which we learn from 4.3 and 4.5. In summary, the replacement scheme for the density matrix consists of the Born approximation, the thermal initial condition for the bath (IC) and the additional replacement 4.8 and reads

$$\rho(s) \xrightarrow[Born]{} \rho_{S}(s) \otimes \rho_{B}(0) \xrightarrow[IC]{} \rho_{S}(s) \otimes \rho_{B}^{\beta} \xrightarrow[4.8]{} \rho_{S}(t) \otimes \rho_{B}^{\beta} , \qquad (4.9)$$

where we skip the formally required  $O(\alpha^2)$  in the last step and end up with an approximant for  $\rho(s)$  which depends on a freely chosen time t, enabling us to make the equation for  $\rho_s$  time-local. Please note, that this approximation only is reasonable when used in the context of 4.4 because there higher order terms will lead to contributions  $O(\alpha^4)$ , which we neglect. Approximating  $\rho(s)$  in general with the above procedure would give us an instant solution to the time evolution of  $\rho$ when choosing t = 0, which obviously would not be useful at all.

After the replacement 4.9, it is possible to split the bath and the system terms and to compute the partial trace over the bath degrees of freedom. Simplifying the resulting expressions algebraically and reparametrizing the integral, we arrive at

$$\dot{\rho_{S}}(t) = - \int_{0}^{t} d\tau \left[ V_{t} \mathcal{A} V_{t-\tau} \mathcal{A} \rho_{S}(t) c(\tau) - V_{t} \mathcal{A} \rho_{S}(t) V_{t-\tau} \mathcal{A} c^{*}(\tau) \right]$$
  
+ h.c. (4.10)

where we used that the thermal expectation values  $\langle (b_k^{\dagger})^2 \rangle_{\beta}$  and  $\langle b_k^2 \rangle_{\beta}$  vanish (c. f. (4.6)), employed the reduced time evolution superoperators  $V_t$  (see 2) and recalled the bath correlation function

$$c(\tau) = tr\left\{V_{t}B^{\dagger}V_{t-\tau}B\,\rho_{B}^{\beta}\right\} + tr\left\{V_{t}B\,V_{t-\tau}B^{\dagger}\,\rho_{B}^{\beta}\right\}.$$
(4.11)

as it was introduced and shown not to depend on the time t, but only on the time difference  $\tau$ , in section 3.1.

Reordering the terms to commutators and introducing yet another shorthand notation, we can condense our result to find the

Weak-Coupling 
$$\dot{\rho_{S}}(t) = [V_{t}K(t) \rho_{S}(t), V_{t}A] + h.c.$$
  
Master Equation with  $K(t) = \int_{0}^{t} d\tau c(\tau) V_{-\tau}A$  (4.12)

It can be seen that influences on the time evolution related to the past are mediated via K(t) alone and that the correlation function plays a major role in controlling the memory of the system in our description, which in particular is important for the Markov approximation below (section 4.2).

We now turn explicitly to our system, enabling us to compute the

above quantities to a more detailed level. First of all, we use the concrete form of  $c(\tau)$ , which was calculated in section 3.1 to read

$$\begin{split} c(\tau) &= \sum_{k=1}^{\infty} \tilde{g}_{k}^{2} \left[ e^{i\tau\Omega_{k}} n(\Omega_{k}) + e^{-i\tau\Omega_{k}} (n(\Omega_{k}) + 1) \right] \\ c(\tau) &= \int_{0}^{\infty} d\omega \, \mathcal{J}(\omega) \left[ e^{i\tau\omega} n(\omega) + e^{-i\tau\omega} (n(\omega) + 1) \right], \end{split}$$

and then we plug in  $\mathcal{A} = \sigma_z$  such that

$$\begin{split} \mathsf{K}(\mathsf{t}) &= \int_0^{\mathsf{t}} \mathsf{d}\tau \, V_{-\tau} \sigma_z \sum_{k=1}^{\infty} \, \tilde{g}_k^2 \left[ (2 \langle \mathsf{n}_k \rangle_\beta + 1) \cos \tau \Omega_k - \mathfrak{i} \sin \tau \Omega_k \right] \\ \mathsf{K}(\mathsf{t}) &= \int_0^{\mathsf{t}} \mathsf{d}\tau \, V_{-\tau} \sigma_z \int_0^{\infty} \mathsf{d}\omega \, J(\omega) \left[ (2\mathsf{n}(\omega) + 1) \cos \tau \omega - \mathfrak{i} \sin \tau \omega \right] \end{split}$$

in the discrete and the continuous description, respectively. We will compute the time evolution using the master equation in the interaction picture but in order to evaluate observables have to return to the Schrödinger picture of course. Due to trace cyclicity this is equivalent to transforming the observable to the interaction picture and we get

$$\rho_{S}^{(s)}(t) = V_{-t}\rho_{S}(t) \Rightarrow \langle O \rangle = tr\{O V_{-t}\rho_{S}(t)\} = tr\{V_{t}O \rho_{S}(t)\}.$$
(4.13)

Up to here, we made use of the Born and the weak-coupling approximation and assumed a thermal initial state of the bath. In the following, two additional approximations are discussed as they are commonly used and we will partially employ them in our work.

## 4.2 MARKOV APPROXIMATION - THE LONG TIME LIMIT

Commonly, *Markovian systems* are characterized by bath correlation functions which decay on a timescale  $\tau_B$  significantly smaller than the relaxation time  $\tau_{rel}$  of the OQS; More precisely, Markovianity characterizes the flow of information from the bath to the system to vanish and consistent measures can be defined to quantify non-Markovianity [9]. Under the assumption  $\tau_B \ll \tau_{rel}$ , we may extend the upper integration boundary in K(t) to  $\infty$ , as we only add contributions for which  $c(\tau)$  is decayed already, suppressing the integrand. Note that this integration extension corresponds to K(t)  $\rightarrow$  K( $\infty$ ) which makes the transition notationally very convenient.

We are going to investigate the influence of the Markov approximation for an exactly solvable reduced system in C. For convenience, we summarize the

$$\begin{array}{ll} \text{Markovian} & \dot{\rho_{S}}(t) = [V_{t}K_{\infty} \ \rho_{S}(t), V_{t}\mathcal{A}] + \text{h.c.} \\ \text{Master Equation} & \text{with} \quad K_{\infty} = \int_{0}^{\infty} d\tau \ c(\tau) \ V_{-\tau}\mathcal{A} \quad (4.14) \end{array}$$

Note that we do not employ the Markov approximation in all cases, as it requires the above assumptions<sup>2</sup> and therefore poses restrictions to

<sup>2</sup> Strictly speaking, it requires assumptions on the decoherence rates, see C.

our system and its parameters. However, staying in the more general non-Markovian setting prevents us from showing complete positivity of the ME, possibly leading to serious flaws in the description of physics [7]. Additionally, we encounter issues regarding the stability of stationary states if we do not work with the MME, which is shown in C as well. As we require a stable description via the master equation in order to approximate the behaviour of the system for further analyses, we will prefer 4.14 over 4.12 for the core computations.

# 4.3 SECULAR APPROXIMATION

The *secular approximation* usually is performed in addition to the Markov approximation, although there is no strict necessity to combine both schemes and we will perform them separately to keep the concepts of both schemes separated from each other. The idea is that for the spectrally decomposed master equation, all contributions with a rapidly oscillating phase may be neglected, where we consider those frequencies large which yield a high number of oscillations during the system's relaxation timescale  $\tau_{rel}$ , intuitively causing the contribution "to average out".

We start the derivation by performing a spectral decomposition of the master equation via an orthonormal eigenbasis  $\{|\alpha\rangle\}_{\alpha=1}^{N}$  of  $H_S$  with corresponding eigenvalues  $E_{\alpha}$ . Expanding the coupling operator  $\mathcal{A}$  in this basis, the ME takes the form

$$\dot{\rho_{S}}(t) = \sum_{a,b,c,d} e^{it(E_{a}-E_{b}+E_{c}-E_{d})} \mathcal{A}_{ab} \mathcal{A}_{cd} [|a\rangle \langle b|\rho_{S}(t),|c\rangle \langle d|] \kappa_{ab}(t)$$

$$+ \text{ h.c. with } \kappa_{ab}(t) = \int_{0}^{t} d\tau \ e^{-i\tau(E_{a}-E_{b})} c(\tau), \qquad (4.15)$$

where each of the four sums runs over the eigenbasis containing  $N = \dim\{H_S\}$  elements and we denoted  $\mathcal{A}_{ab} = \langle a | \mathcal{A} | b \rangle$ .

The secular approximation, closely related to the *rotating wave approximation* in quantum optics,<sup>3</sup> then states that for relatively big energy terms in the first exponential, many oscillations occur during characteristic time scales of the system dynamics. More formally, the assumption reads

$$\mathsf{E}_{a} - \mathsf{E}_{b} + \mathsf{E}_{c} - \mathsf{E}_{d} \gg \frac{2\pi}{\tau_{\mathrm{rel}}} \quad \text{for} \quad \mathsf{E}_{a} - \mathsf{E}_{b} + \mathsf{E}_{c} - \mathsf{E}_{d} \neq 0. \tag{4.16}$$

The approximation is performed by neglecting all the terms containing a non-vanishing phase in the first exponential, which corresponds to the replacement

$$e^{it(E_a - E_b + E_c - E_d)} \rightarrow \delta_{E_a - E_b + E_c - E_d,0}.$$
(4.17)

<sup>3</sup> In quantum optical systems, the difference between the secular and the rotating wave approximation is restricted to the Lamb shift Hamiltonian H<sub>LS</sub>, c. f. 4.18.

We finally note that the combination of the Markov and the rotating wave approximation amounts to replacing the upper integration boundary in (4.15) by  $\infty$  in addition to the replacement (4.17).

We briefly want to state that for the full set of approximations of the master equation, one arrives at a time-local differential equation with constant decoherence rates which can be brought into *Lindblad form* 

$$\dot{\rho_S}(t) = -i[H_{LS}, \rho_S(t)] + \sum_{k=1}^{N^2-1} \gamma_k \left( A_k \rho_S(t) A_k^\dagger - \frac{1}{2} \{ A_k^\dagger A_k, \rho_S(t) \} \right)$$

It can be shown that this equation describes diagonal elements (populations) and off-diagonal terms (coherences) of  $\rho_S$  separately, which is possible because in the secular approximation the corresponding coupling terms are neglected. Furthermore, complete positivity, trace-preservedness and energy conservation are guaranteed (c. f. appendix C and [31]), making the mathematical description via the Lindblad form physically feasable. These properties can be shown to extend to the non-Markovian Master Equation (nMME) under the condition of positivity of the rates  $\gamma$ , which are time-dependent in the nMME.

## 4.4 STATIONARITY OF THE THERMAL SYSTEM STATE

As mentioned above in section 4.2 and elaborated in more detail in appendix C, the Markov approximation has both, valuable advantages and severe drawbacks, and the question whether to invoke it or not is non-trivial. Here we want to give one reason why to be careful with the approximation for our numerical analysis, where we prepare a system for DMRG based on the approximative description with the master equation. This is done in two steps by first proving the stationarity of the thermal system state in the Markovian master equation and then showing that stationarity is violated in the non-Markovian description by giving numerical counterexamples.<sup>4</sup> This discrepancy is then investigated via DMRG analysis, which provides us with a numerically exact solution of the time evolution.<sup>5</sup>

Let us start with a useful identity of the bath correlation function needed for the proof of Markovian stationarity: The Bose-Einstein distribution n fulfils

$$n(\omega) + 1 = \frac{1 + e^{\beta \omega} - 1}{e^{\beta \omega} - 1} = e^{\beta \omega} n(\omega)$$
(4.18)

<sup>4</sup> For both, the Markovian and the non-approximated description, we will use the secular approximation.

<sup>5</sup> We additionally were able to test the validity of DMRG for small toy models by comparing it to exact diagonalization computations, which is skipped here for convenience as it is a minor consistency check

which yields the identity

$$c(-\tau - i\beta) = \int_{0}^{\infty} d\omega \, \mathcal{J}(\omega) \left[ e^{-i\tau\omega} e^{\beta\omega} n(\omega) + e^{i\tau\omega} e^{-\beta\omega} (n(\omega) + 1) \right]$$
  
=  $c(\tau).$  (4.19)

In the secular approximated master equation, c enters via the "rates"  $\kappa_{ab}$ , which in the Markovian description have the key feature

$$e^{-\beta E_{b}} \kappa_{ab}(\infty) = \int_{0}^{\infty} d\tau \ e^{-\beta E_{b}} e^{-i\tau(E_{a}-E_{b})} c(\tau)$$
  
$$= \int_{-i\beta}^{\infty} d\tau' \ e^{-\beta E_{b}} e^{i\tau'(E_{a}-E_{b})} e^{-\beta(E_{a}-E_{b})} c(\tau') \quad (4.20)$$
  
$$= e^{-\beta E_{a}} \kappa_{ba}(\infty) + i e^{-\beta E_{a}} \int_{0}^{\beta} d\tau'' \ e^{\tau''(E_{a}-E_{b})} c(-i\tau'')$$

where we performed the replacements  $\tau \rightarrow \tau' = -\tau - i\beta$  and  $\tau' \rightarrow \tau'' = i\tau'$ , used 4.19 and were allowed to choose a path for the complex integration freely as the integrand does not have singularities. Now, note that c(x) is real for a purely imaginary argument, making the second term in the last line purely imaginary. Then it is clear that

$$e^{-\beta \mathsf{E}_{b}}(\kappa_{ab}(\infty) + \kappa^{*}_{ab}(\infty)) = e^{-\beta \mathsf{E}_{a}}(\kappa_{ba}(\infty) + \kappa^{*}_{ba}(\infty)). \quad (4.21)$$

It is important to see, that an additional contribution from the integral into the imaginary direction but at some finite real part t of the integration boundaries would *not* vanish in the same way as the last term in 4.20, showing that for a relation similar to 4.21 to hold, the time limit  $t \rightarrow \infty$  is necessary, and that therefore, the nMME in general will not exhibit this property.

We now can turn to the master equation itself and compute for the thermal initial system state  $\rho_S^{(th)} = \mathcal{Z}_S^{-1} e^{-\beta H_S}$  at inverse bath temperature  $\beta$ ,

$$\dot{\rho_{S}}^{(th)} = \sum_{a,b,c,d} \delta_{E_{a}-E_{b}+E_{c}-E_{d},0} \mathcal{A}_{ab}\mathcal{A}_{cd} \qquad (4.22)$$

$$\times [|a\rangle\langle b|\rho_{S}^{(th)},|c\rangle\langle d|]\kappa_{ab}(\infty) + h.c.$$

$$= \sum_{a,b} e^{-\beta E_{b}}\kappa_{ab}(\infty) [\sum_{d} \delta_{E_{a},E_{d}}\mathcal{A}_{ab}\mathcal{A}_{bd}|a\rangle\langle d|$$

$$-\sum_{c} \delta_{E_{c},E_{b}}\mathcal{A}_{ab}\mathcal{A}_{ca}|c\rangle\langle b|] + h.c.$$

$$\stackrel{6}{=} \sum_{a,b} e^{-\beta E_{b}} [(\kappa_{ab}(\infty) + \kappa_{ab}^{*}(\infty))\sum_{d} \mathcal{A}_{ab}\mathcal{A}_{bd}|a\rangle\langle d|\delta_{E_{a},E_{d}}$$

$$-(\kappa_{ab}(\infty) + \kappa_{ab}^{*}(\infty))\sum_{c} \mathcal{A}_{ab}\mathcal{A}_{ca}|c\rangle\langle b|\delta_{E_{b},E_{c}}]$$

$$= \sum_{a,b} K_{ab} \sum_{d} [\mathcal{A}_{ab}\mathcal{A}_{bd}|a\rangle\langle d|\delta_{E_{a},E_{d}} - \mathcal{A}_{ab}\mathcal{A}_{da}|d\rangle\langle b|\delta_{E_{b},E_{d}}],$$

which is skew-Hermitian because, using the abbreviation  $K_{ab} = e^{-\beta E_b}(\kappa_{ab}(\infty) + \kappa^*_{ab}(\infty))$ ,  $K_{ab} = K_{ba}$  holds via 4.21. At the same time, it can be seen easily e.g. from the first line in 4.22 that  $\rho_S$  is Hermitian, such that we find

$$\dot{\rho_{S}}^{(th)} = \dot{\rho_{S}}^{(th)^{\dagger}} = -\dot{\rho_{S}}^{(th)} \Rightarrow \dot{\rho_{S}}^{(th)} = 0.$$
 (4.23)

Thus, we know the thermal system state to be stationary in the fully approximated system, i. e. when invoking the Born, the weak-coupling, the secular and the Markov approximation.

In the second part we want to show a numeric example of the nonsecular master equation which does not exhibit the thermal stationarity property. To this extend, we turn to the system introduced as spinboson-model in chapter 2 and initialize the OQS, which now is a single spin, to be in its thermal state  $\rho_S^\beta$  at the same temperature as the bath for the following parameters:

$$\begin{split} \omega_{\rm c} &= 0.3 \; eV \; \omega_{\rm cut} = 0.6 \; eV \qquad s = 1 \; \omega_{\rm S} = 0.3 \; eV \quad (4.24) \\ \Delta &= 0.3 \; eV \qquad \beta = 100 \; eV^{-1} \\ \text{DMRG:} \; m_{\rm bath} = 30 \qquad m_{\rm trunc} = 100 \end{split}$$

We then can numerically solve different master equations and observe the behaviour in fig. 4.1, where the trace distance between the current density matrix of the spin and the thermal initial state is used as a measure to analyze the time evolution.

First, we can look at the secular MME results (orange, dashed) for the thermal initial state which confirm the analytic result in 4.23 as there is no movement away from the thermal state. Furthermore, the secular nMME (blue, dashed) is seen to coincide with this time evolution, although this is proven analytically for the Markovian framework (see above).

Next, we consider the non-secular MME solution (orange, solid), exhibiting initial dynamics with which the open system moves away from the thermal state and therefore denies its stationarity. Again, we can go back to the non-Markovian framework and indeed observe the same dynamics for the non-secular nMME (blue, solid).

In order to evaluate the two different results of the four approximative schemes, we employ the DMRG simulation (yellow) and compare it to the ME results. The initial dynamics are poorly described by the master equation but we observe qualitatively similar dynamics for the non-secular predictions and the numerically exact time evolution, with a phase shift in the oscillations. This tells us that effectively, the weak-coupling approximation is not suitable for the given temperature with  $\beta = 100 \text{ eV}^{-1}$ . However, we want to emphasize that the

<sup>6</sup> Note that  $\kappa_{ab}$  only depends on  $E_a$  and  $E_b$  but not on the particular a or b, making the  $\delta_{E_i,E_i}$  act correctly on  $\kappa_{ij}$ .



Figure 4.1: Time evolution of the spin starting from  $\rho_S^{\beta}$  at the initial bath temperature  $\beta$  as predicted by the nMME, the MME and by DMRG for parameters given in 4.24. For the ME approach the non-secular (solid) and the secular (dashed) results are shown.

damped oscillation towards a constant value of the trace distance, which is visible for both, the DMRG and the ME dynamics, coincide well in shape and w.r.t. their approximate decaying envelope, such that convergence towards the same (pseudo-)stationary state is predicted. Only for longer times a deviation from this simple behaviour is seen in the DMRG simulation. This effect shall be left for further investigation in future works.

We therefore conclude that for our system major changes can occur when employing the common approximations and consequently we will use the non-secular nMME whenever feasable. Mainly it will serve to compare to the numerical results from DMRG and to estimate parameters such as the truncation of the bath modes and the relaxation time and therefore the necessary revival time  $\tau_{rev}$  and the corresponding bath size L. A further review of the temperature influence on the secular approximation is included in section 6.7.

# DENSITY MATRIX RENORMALIZATION GROUP

Here we want to give a very brief introduction to the DMRG as tool to evaluate the predictions made by the master equation(s) above and as a numerically exact procedure serving us to simulate the entire system dynamics at an arbitrary precision. We will include a review of the necessary concepts on Matrix Product States (MPSs) and Matrix Product Operators (MPOs) as they are used to perform our DMRG analyses, but merely constrain ourselves to some key features.

We will mainly follow [39] in this chapter, as we precisely need DMRG applied to matrix product states. Furthermore, we will restrict to the relevant techniques to perform time evolution within DMRG although the setup is able to solve many other tasks as well.

The numerical implementation of all DMRG calculations throughout this project is carried out using the SyTeN-toolkit by Claudius Hubig et al [24, 25].

## 5.1 MATRIX PRODUCT STATES AND OPERATORS

Although an excellent overview of the topic is given in [39], we want to introduce some notions on MPS's and MPO's in order to better understand the precision of results gained with DMRG on one hand and to show how the mixed initial state of our system can be implemented on the other hand. Let us start with a Hilbert space  $\mathcal{H}$  composed of multiple subspaces  $\{\mathcal{H}_i\}_{i=1}^N$  via the tensor product. These subspaces typically correspond to different sites of a chain-like setup, which is not a restriction to specific systems<sup>1</sup> but for us serves an illustrative purpose and in general can be used for the categorization of the system (not applicable in our case), e. g. via the range of interactions or the distribution of the interaction parameters between the sites.

For this composite Hilbert space, a pure state takes the general form

$$|\psi\rangle = \sum_{k_{i}=1}^{\dim \mathcal{H}_{i}} \Psi_{k_{1}...k_{N}} \bigotimes_{i=1}^{N} |k_{i}\rangle_{\mathcal{H}_{i}}$$
(5.1)

which we need for a two-component separation into space A and B, mainly:

$$|\psi\rangle = \sum_{i=1}^{\dim A} \sum_{j=1}^{\dim B} \Psi_{ab} |i\rangle_A \otimes |j\rangle_B$$
 (5.2)

<sup>1</sup> Assuming a chain shape actually is far from our system 2.5 although a unitary map exists which transforms the given *star configuration* into a nearest-neighbour interacting chain.

The single  $|k_i\rangle$  and  $|a, b\rangle$  are elements of an orthonormal basis for the respective space and  $\Psi$  can be understood as a tensor in the former or a common matrix in the latter case. The goal is now to transform this representation into a local notion of the coefficients  $\Psi_{ab}$ , which can be done via a Singular Value Decomposition (SVD) of  $\Psi$ :

It is known [39] that for each rectangular matrix M a decomposition U S V<sup>†</sup> exists, such that S is a non-negative diagonal matrix with rank  $r \leq \max\{\dim A, \dim B\}$ , containing the *singular values*  $\{s_a\}_{a=1}^r$ . This enables us to rewrite 5.2 in its *Schmidt decomposed* form

$$|\psi\rangle = \sum_{\alpha=1}^{r} s_{\alpha} |\alpha\rangle_{A} \otimes |\alpha\rangle_{B}$$
(5.3)

where we defined  $|a\rangle_A = \sum_{i=1}^{\dim A} U_{ia} |i\rangle_A$  and likewise for  $|a\rangle_B$  using  $V^{\dagger}$ .<sup>2</sup> The above procedure can be repeatedly applied to an arbitrary state as in 5.1 by splitting the overall Hilbert space into subsequent bipartitions, starting with  $A = \mathcal{H}_1$ ,  $B = \bigotimes_{i=2}^N \mathcal{H}_i$  and ending with  $A = \mathcal{H}_{N-1}$ ,  $B = \mathcal{H}_N$ . In this way, we can assign a matrix  $A^a$  to each site  $\mathcal{H}_a$ , where the product of all A reproduces  $\Psi_{k1...k_N}$ . If now the problem is high-dimensional and thus computationally very expensive, one can truncate the singular value matrix S in the above decomposition such that the size of the system is reduced significantly. The error introduced by this truncation can for example be controlled by setting a truncation threshold for the singular values, setting a scale to the introduced error. We do not want to go more into detail here, but refer to the literature for details.

In order to compute system dynamics, the time evolution operator has to be applied to the MPS describing the initial state. Therefore it is mandatory to rewrite oprators in a matrix product form as well. This shall not be discussed here either but can be found for example in [39], together with details on normalization of matrix product states and the prescription of purification for general settings. The application of the latter concept to our case is shown in the following section.

#### 5.2 PURIFICATION

In order to describe mixed states, which can not be written in the form 5.1, we will make use of the so-called *purification* prescription, which amounts to copying the system under consideration and interlacing the sites of both copies. With this system, mixed states can be incorporated as we show using the example of a thermal state for a single bosonic

<sup>2</sup> Please note the abuse of notation as we distinguish fundamentally different sets of states on the same subspace only by using a different index. This will not become a severe problem in the following.

mode k with energy  $\Omega_k$ . Denoting the original system with indices P and the copy with Q, such a state has the form

$$|\psi_{k}^{(th)}\rangle = \sqrt{\mathcal{Z}_{k}}^{-1} \sum_{n_{k}} e^{-\beta \Omega_{k} n_{k}/2} |n_{k}\rangle_{P} \otimes |n_{k}\rangle_{Q}$$
(5.4)

but as one can see, the local structure of a matrix product state is not achieved yet because the indices of the physical and the auxiliary site are fixed to be the same. In a collection of bosonic modes, we instead would arrive at a state structure of blocks containing two sites each, corresponding to the physical and the copied site for each mode. We therefore rewrite the state coefficients as product which yields

$$|\psi_{k}^{(th)}\rangle = \sqrt{\mathcal{Z}_{k}}^{-1} \sum_{a,n_{k},n_{k}'} \delta_{n_{k},a} e^{-\beta \Omega_{k}a/2} \delta_{a,n_{k}'} |n_{k}\rangle_{P} |n_{k}'\rangle_{Q}$$
(5.5)

for which we are able to separate the different single-site matrices. Please note that due to the standard description of the bosonic mode in the eigen basis of its Hamiltonian, the thermal state density matrix is diagonal and the single-site matrices in the above decomposition take their fairly simple form. In contrast to this, for the two-level system included in our system and for detuning frequencies  $\Delta \neq 0$  the single-site matrices contain the transformation matrix between the energy eigen basis and the basis in which the Hilbert space is described, i. e. the eigen basis of  $\sigma_z$ , such that they become more complicated and the splitting procedure does not appear in an artificial form like 5.5. The same holds for the initial state of the cavity if it is found in a truly quantum mechanical state composed of multiple eigen states of the Hamiltonian. The corresponding prescriptions can be computed in general for the spin and the cavity at fixed dimension:

$$|\varphi_{spin}\rangle = \sum_{b,\sigma,\sigma'} U_{\sigma b} s_b U_{\sigma' b} |\sigma\rangle_P |\sigma'\rangle_Q$$
 (5.6)

$$|\varphi_{cvty}\rangle = \sum_{c,n_l,n_l'} V_{n_lc} S_c V_{n_l'c} |n_l\rangle_P |n_l'\rangle_Q$$
(5.7)

where s ad S denote the eigenvalues of the initial state density matrix of the spin and cavity, respectively, which for a pure state are 1 (multiplicity 1) and 0 (remaining multiplicity). The matrices U and V are the unitary transformation matrices between the respective eigen basis of the density matrix and the basis of description, acting as e. g.  $|b\rangle = \sum_{\sigma} U_{\sigma b} |\sigma\rangle$ . Depending on whether the initial MPS is wanted to be left- or right-normalized, one then separates the factors in 5.5 - 5.7 into the two on-site matrices for the MPS and (for our choice of left-normalization) arrives at

$$(A_{P,cvty})^{n_{l}}{}_{1,c} = V_{n_{l}c} \quad (A_{Q,cvty})^{n'_{l}}{}_{c,1} = V_{n'_{l}c} S_{c}$$

$$(A_{P,spin})^{\sigma}{}_{1,b} = U_{\sigma b} \quad (A_{Q,spin})^{\sigma'}{}_{b,1} = U_{\sigma' b} s_{b} \qquad (5.8)$$

$$(A_{P,k})^{n_{k}}{}_{1,a} = \delta_{n_{k}a} \quad (A_{Q,k})^{n'_{k}}{}_{a,1} = \sqrt{\mathcal{Z}_{k}}^{-1} e^{-\beta \Omega_{k} a/2} \delta_{n'_{k}a}$$

This result can then be implemented immediately for DMRG simulations. It should be noted, that there is no closed form for the transformation matrices V as its dimension depends on the chosen truncation on the cavity mode Hilbert space.

#### 5.3 TIME EVOLUTION METHODS

Throughout our simulations, two time evolution methods will be used in combination, exploiting the advantages of each concept.

Simulation starts by employing the *Krylov method*, which refers to the strategy of how the time evolution operator is applied and the massive amount of matrix-matrix multiplications can be handled efficiently, using the Krylov subspace to compute the eigenbasis and -values at each time step. We will not go into detail on these methods but refer to literature on the numerics used in the library [16, 21].

While the Krylov method is able to produce as exact results as required and can be controlled very well, it is rather slow, becoming very computationally time-expensive for highly entangled states with large bond dimensions. Therefore, a second method is used to perform the subsequent time evolution, making use of the time-dependent variational principle Time-Dependent Variational Principle (TDVP), as it was introduced in [19]. Here, the errors are not controlled as nicely (regarding the implementation in the library) but this method is significantly faster, enabling us to explore bigger time scales. The reason for the above composite procedure is that TDVP induces rather large errors for low entangled states, for single site TDVP the entanglement even is constrained via a fixed maximal bond dimension. We therefore start with a Krylov time evolution to build up entanglement and after reaching a desired maximal bond dimension to which we truncate anyways, we switch to the faster single-site TDVP method.

#### 5.4 PARAMETERS

The topic of parameter choice is a very involved one for DMRG because wrongly chosen settings will easily disturb the result by inducing truncation of relevant contributions. Therefore we briefly want to mention the parameters and our standard choice for them.

First of all we introduce the truncation threshold  $r_{trunc}$ , which describes the minimal matrix element contribution that is considered in the MPS calculations. It is an implemented setting in the SYTEN toolkit and we will set it at  $10^{-6}$ , a setting which we occasionally will check to yield convergence.

The second parameter is responsible for truncating the matrices at the bonds between the sites as well; The truncation dimension  $m_{trunc}$  is the maximal dimension until which the exact bond matrix is kept (up to the threshold truncation with  $r_{trunc}$ ) and all occuring bigger

matrices are truncated back to the size  $m_{trunc}$ . Typical settings for this will be 100 to 400 - depending on the size and local dimension of the bath.

The last parameter is the local bath dimension  $m_{bath}$ , which is discussed in section 3.3 already and will be chosen problem-dependently.

# Part II

# TIME EVOLUTION AND THERMALIZATION

With a rich toolbox at hand, which allows us to investigate the time evolution of the introduced systems, we turn to the second part. While the first chapter 6 serves the purpose of evaluating the introduced methods and establishing their numerical implementation by treating an analytically solvable subsystem, the second chapter 7 contains our results on the full system dynamics and the thermalization of the cavity mode. The topic of quantum decoherence and relevant insights on the nature of the real-world systems are presented there as well.

# 6

# A LONELY DYE MOLECULE

Before turning to the final core topic of our project, we want to examine the system dynamics of a subsystem of the general setting, introduced in chapter 2 and described by 2.6. The special case of  $\Delta = 0$  will be of particular interest and we will focus on this setting in order to establish the equations and methods derived in part i. Regarding the physical context, the spin-boson model corresponds to a single dye molecule, of which we investigate a single resonant two-level DOF in interaction with its rovibrational modes. The simplified situation is depicted in fig. 6.1, with the cavity being excluded from our description in this chapter.



Figure 6.1: Physical system equivalent to the setup treated in chapter 6. Only a single dye molecule is investigated, corresponding to electronic and rovibrational DOFs. Figure adapted from [36].

# 6.1 THE PURE DEPHASING MODEL

In this section, we look at the spin-boson model for the special case of *pure dephasing*, that is we set  $\Delta = 0$  and analyse the consequences of this particular choice for the system dynamics. The open system Hamiltonian, having been reduced for the spin-boson system already, now takes the simple form

$$H_{\rm S} = \frac{\omega_{\rm S}}{2} \sigma_z \,. \tag{6.1}$$

An analytical solution for the time evolution of the open system has been derived before  $[5, 22]^1$  such that we can test approximation schemes like the ones introduced in chapter 4 and the numerical procedures which we will implement. The spin dynamics will reveal the origin of the name *pure dephasing*, as the two-level system only relaxes its  $\langle \sigma_x \rangle$ -excitation but remains at fixed energy, proportional

<sup>1</sup> Section A.2. in [5] and II.A. in [22]

to  $\langle \sigma_z \rangle$ . We want to rederive this exact solution, following [5] but correcting for some mistakes, finding the solution in [22] for the particular choice  $\alpha = 1$ . Afterwards we evaluate the master equation for this reduced model.

# 6.2 ANALYTIC SOLUTION

We begin by stating the Dyson formula for the unitary time-evolution operator and introducing the Magnus Expansion, which can be taken from [6], chapter 2, and replaces the time ordered Dyson series as

$$U(t) = T_{\leftarrow} \exp\left[-i \int_0^t ds \ H_I(s)\right] \longrightarrow \exp[\Omega(t)]$$

 $\Omega(t)$  can be computed using the formula <sup>2</sup>

$$\Omega(t) = -i \int_0^t dt_1 \ H_I(t_1) - \frac{1}{2} \int_0^t dt_1 \ \int_0^{t_1} dt_2 \ [H_I(t_1), H_I(t_2)] + O(H_I^3)$$

and U(t) is then evaluated by plugging in the interaction Hamiltonian as follows: We write down the time evolution of  $H_I$  in the interaction picture reading<sup>3</sup>

$$\begin{aligned} H_{I}(t) &= e^{i(H_{S}+H_{B})t}H_{I}e^{-i(H_{S}+H_{B})t} & (6.2) \\ &= \sigma_{z}\sum_{k=1}^{\infty} \tilde{g}_{k}\left(e^{iH_{B}t}b_{k}e^{-iH_{B}t} + e^{iH_{B}t}b_{k}^{\dagger}e^{-iH_{B}t}\right) \\ &= \sigma_{z}\sum_{k=1}^{\infty} \tilde{g}_{k}(e^{-i\Omega_{k}t}b_{k} + e^{i\Omega_{k}t}b_{k}^{\dagger}) \,. \end{aligned}$$

Next, this expression is used to compute the commutator

$$[H_{I}(t_{1}), H_{I}(t_{2})] = \mathcal{O}([\sigma_{z}, \sigma_{z}]) + \sigma_{z}^{2} \sum_{k,l} \tilde{g}_{k} \tilde{g}_{l} \left( \mathcal{O}([b_{k}, b_{l}]) + \mathcal{O}\left([b_{k}^{\dagger}, b_{l}^{\dagger}]\right) + e^{i(\Omega_{k}t_{1} - \omega_{1}t_{2})}[b_{k}^{\dagger}, b_{l}^{\dagger}] + e^{i(\Omega_{k}t_{1} - \omega_{1}t_{2})}[b_{k}^{\dagger}, b_{l}] \right)$$

$$= -2i \sum_{k=1}^{\infty} \tilde{g}_{k}^{2} \sin(\Omega_{k}(t_{1} - t_{2})) \mathbb{1}_{S,B}$$

$$(6.3)$$

confirming (A3.1) (equation after (A3)) in [5]. Returning to the Magnus expansion, we then get:

$$\begin{split} \Omega(t) &= -i \int_{0}^{t} dt_{1} \ H_{I}(t_{1}) - \frac{1}{2} \int_{0}^{t} dt_{1} \ \int_{0}^{t_{1}} dt_{2} \ [H_{I}(t_{1}), H_{I}(t_{2})] \\ &= \sigma_{z} \sum_{k=1}^{\infty} \ \tilde{g}_{k}(\alpha_{k}(t)b_{k}^{\dagger} - \alpha_{k}^{*}(t)b_{k}) - i\mathbb{1}_{S,B} \ tf(t) \end{split}$$

<sup>2</sup> Please note that [5] uses a different relative sign, this is found to be a confusion with the prefactor  $(-i)^2$  and is corrected here.

<sup>3</sup> differing from (A<sub>3</sub>) in [5] by the corrected exponent in the second summand.

where we used (6.2) and (6.3) and defined

$$\alpha_{k}(t) = \tilde{g}_{k} \frac{1 - e^{i\Omega_{k}t}}{\Omega_{k}} \quad f(t) = \frac{1}{t} \sum_{k} \frac{\tilde{g}_{k}^{2}}{\Omega_{k}^{2}} (\Omega_{k}t - \sin(\Omega_{k}t))$$

corresponding to (A5) in [5]. Please note that the above result for  $\Omega(t)$  is *exact*, as the higher order contributions consist of iterated commutators and  $[H_I(t_1), H_I(t_2)] \propto \mathbbm{1}_{S,B}$ , setting all higher order terms to 0. Afterwards, we can decompose the time evolution operator, which is diagonal in the spin subspace because  $\Omega(t)$  is, i. e.  $U(t) = \sum_{\pm} U_{\pm}(t) |\pm\rangle \langle \pm |$  and can write

$$U_{\pm}(t) = \exp\left[-i\mathbb{1}_{B}tf(t) \pm \sum_{k} \tilde{g}_{k}(\alpha_{k}(t)b_{k}^{\dagger} - \alpha_{k}^{*}(t)b_{k})\right]$$
(6.4)

confirming (A4) in [5]. We now continue to compute the decay rate  $\Gamma_b$  introduced via  $\rho_S^{+-}(t) = e^{-t\Gamma_b(t)}\rho_S^{+-}(0)$  as it is carried out in the main part of [5] by using the periodicity of the trace:

$$\begin{split} \Gamma_{b}(t) &= -\frac{1}{t} \ln \left( tr_{B} \left\{ U_{+}^{\dagger}(t) \rho_{B}(0) U_{-}(t) \right\} \right) \\ &= -\frac{1}{t} \ln \left( tr_{B} \left\{ \rho_{B}(0) \right. \right. \right. \\ &\times exp \left[ -i \mathbb{1}_{B} tf(t) - \sum_{k=1}^{\infty} \tilde{g}_{k}(\alpha_{k}(t) b_{k}^{\dagger} - \alpha_{k}^{*}(t) b_{k})) \right] \\ &\times exp \left[ i \mathbb{1}_{B} tf(t) - \sum_{k=1}^{\infty} \tilde{g}_{k}(\alpha_{k}(t) b_{k}^{\dagger} - \alpha_{k}^{*}(t) b_{k})) \right] \right\} \end{split}$$
(6.5)

As we have  $[\mathbb{1}_B, \mathfrak{b}_k^{\dagger}] = [\mathbb{1}_B, \mathfrak{b}_k] = 0$ , the exponentials can easily be decomposed and recombined such that the first terms in the exponents cancel and the second ones add up such that

$$\Gamma_{b}(t) = -\frac{1}{t} \ln \left( tr_{B} \left\{ \rho_{B}(0) \exp \left[ 2 \sum_{k=1}^{\infty} \tilde{g}_{k}(\alpha_{k}^{*}(t)b_{k} - h.c.) \right] \right\} \right),$$

which then can be converted via a more involved computation of the partial trace to yield

$$\Gamma_{b}(t) = \frac{1}{t} \sum_{k=1}^{\infty} \tilde{g}_{k}^{2} \, 8 \coth\left(\frac{\beta\Omega_{k}}{2}\right) \frac{\sin^{2}(\Omega_{k}t/2)}{\Omega_{k}^{2}}, \tag{6.6}$$

coinciding with (4) in [22] for  $\alpha = 1.4$  Making use of the spectral density replacement 3.3, we write the decay rate as

$$\Gamma_{\rm b}(t) = \frac{8}{t} \int_0^\infty d\omega J(\omega) \coth\left(\frac{\beta\omega}{2}\right) \frac{\sin^2(\omega t/2)}{\omega^2}.$$
 (6.7)

<sup>4</sup> One uses the trigonometric identity  $1 - \cos x = 2\sin^2(x/2)$  and corrects for the deviation in the definition of  $\Gamma_b(t)$  between [5] and [22] and actually recieves a slightly different result than (9) in [5]

We finalize this review by evaluating the resulting time evolution of  $\langle \sigma_x \rangle$  and  $\langle \sigma_z \rangle$ . Transforming back to the Schrödinger picture (or equivalently transforming  $\sigma_x$  to the interaction picture), we can write

$$\langle \sigma_{\mathbf{x}} \rangle (\mathbf{t}) = \operatorname{tr} \left\{ \sigma_{\mathbf{x}} e^{-i\mathbf{t}H_{S}} \rho_{S}(\mathbf{t}) e^{i\mathbf{t}H_{S}} \right\}$$
  
=  $\rho_{S}^{+-}(\mathbf{t}) e^{-i\mathbf{t}\omega_{S}} + \rho_{S}^{-+}(\mathbf{t}) e^{i\mathbf{t}\omega_{S}}$   
=  $e^{-\Gamma_{b}(\mathbf{t})\mathbf{t}} 2\mathfrak{Re} \left\{ \rho_{S}^{+-}(\mathbf{0}) e^{-i\mathbf{t}\omega_{S}} \right\} .$  (6.8)

Likewise, we can compute  $\langle \sigma_z \rangle$  (t) based on the diagonal analogue of  $\Gamma_b(t)$ , which can be easily seen to be 1 (the exponentials cancel each other out). We therefore simply get

$$\langle \sigma_z \rangle (\mathbf{t}) = \operatorname{tr} \left\{ \sigma_z e^{-i \mathbf{t} H_S} \rho_S(\mathbf{t}) e^{i \mathbf{t} H_S} \right\}$$
  
=  $\rho_S^{++}(\mathbf{0}) - \rho_S^{--}(\mathbf{0})$  (6.9)  
=  $\langle \sigma_z \rangle (\mathbf{0})$ 

that is the energy of the spin does not change throughout the time evolution. This motivates the name *pure dephasing model* as the entire system dynamics lie in the  $\langle \sigma_x \rangle$  excitation.

As a side remark, we want to note that due to the fixed spin energy, corresponding to a fixed occupation of the states  $|\pm\rangle$ , thermalization is not possible in the pure dephasing case unless the initial state was tuned to have the thermal diagonal elements and arbitrary off-diagonal elements, which then would decay.

## 6.3 MASTER EQUATION

For the specific setup of the pure dephasing model, the master equation can be simplified and the explicit weak-coupling approximation corresponding to 4.8 is incorporated at a scalar rather than the density matrix level, reduced to the comparison of two ordinary differential equations.

Let us start with the Born master equation and compute<sup>5</sup>

$$\dot{\rho_{S}}(t) = -\int_{0}^{t} d\tau \qquad [\rho_{S}(\tau)c(\tau) - \sigma_{z}\rho_{S}(\tau)\sigma_{z}c^{*}(\tau) + \rho_{S}(\tau)c^{*}(\tau) - \sigma_{z}\rho_{S}(\tau)\sigma_{z}c(\tau)]$$
$$= -\int_{0}^{t} d\tau \qquad 2\mathfrak{Re}\{c(\tau)\}[\rho_{S}(\tau) - \sigma_{z}\rho_{S}(\tau)\sigma_{z}] \qquad (6.10)$$

<sup>5</sup> Please note that employing the Born approximation already goes along with assuming a weak coupling  $\alpha$ .

where we used  $\sigma_z^2 = \mathbb{1}_2$  and the fact that  $[H_S, \sigma_z] = 0$  allowed us to skip the time evolution of  $\sigma_z$ . Similarly to the analytic solution above, we evaluate the master equation componentwise and write

$$\begin{split} \dot{\rho_{S}}^{\pm\pm}(t) &= -\int_{0}^{t} d\tau \ 2\Re e\{c(\tau)\} \rho_{S}^{\pm\pm}(\tau)(1-(\pm 1)^{2}) = 0 \\ \dot{\rho_{S}}^{\pm\mp}(t) &= -\int_{0}^{t} d\tau \ 2\Re e\{c(\tau)\} \rho_{S}^{\pm\mp}(\tau)(1-(\pm 1)(\mp 1)) \\ &= -4\int_{0}^{t} d\tau \ \Re e\{c(\tau)\} \rho_{S}^{\pm\mp}(\tau) \end{split}$$
(6.11)

leaving us with a single (non-trivial) scalar differential equation. In the weak coupling case one can now easily substitute  $\rho_S^{\pm\mp}(\tau)$  with  $\rho_S^{\pm\mp}(t)$ , simplifying the master equation from an ODE of second to one of first order. This can be seen by taking the derivative of the non-approximated equation and comparing both<sup>6</sup>

NON-WEAK 
$$(\dot{\rho}_{S}^{\pm\mp})_{NW}(t) = -4\Re \epsilon \{c(t)\} \rho_{S}^{\pm\mp}(t)$$
 (6.12)

WEAK 
$$(\dot{\rho_{S}}^{\pm\mp})_{W}(t) = -4\mathfrak{Re}\{C(t)\}\rho_{S}^{\pm\mp}(t)$$
 (6.13)

where we wrote the integral over c as C in order to demonstrate the similarity. By iterating the second equation and subtracting the non-approximated version, we can boil down the difference in the second order ODE to

$$(\dot{\rho}_{S}^{\pm\mp})_{NW}(t) - (\dot{\rho}_{S}^{\pm\mp})_{W}(t) = -16 \left(\Re e\{C(t)\}\right)^{2} \rho_{S}^{\pm\mp}(t) \qquad (6.14)$$

which in the Markovian limit  $C(t) \rightarrow C(\infty)$  can be identified to give an oscillating contribution of frequency  $4\Re \mathfrak{e} \{C(\infty)\}$ .

We will use these results and the existence of an analytic solution for the spin-boson model to understand the effects of approximations and to test numerical procedures used throughout the present work. Note that for the case  $\Delta \neq 0$  there is no similar analytic solution because 6.3 does not hold and therefore the Magnus expansion is not finite. We now continue by briefly describing the DMRG setup for the reduced model.

# 6.4 DENSITY MATRIX RENORMALIZATION GROUP

For the pure dephasing model, the DMRG implementation is straight forward when using the concepts introduced in chapter 5, in particular we use the purification prescription in order to initialize the bosonic bath in a thermal state. The initial state of the two-level system on the

<sup>6</sup> We here refer to the result in 6.11 as non-approximated or non-weak although the Born ME is not exact.

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other hand is given by three independent real parameters a,  $b_1$  and  $b_2$  as can be seen from hermiticity and normalization of  $\rho_S$ :

$$\rho_{S}(0) = \begin{pmatrix} a & b_1 + ib_2 \\ b_1 - ib_2 & 1 - a \end{pmatrix}$$
(6.15)

When restricting to a pure state with real coefficients, the initial state even is to be described by a single parameter  $\alpha \in \mathbb{R}$ , as can be seen via

$$|\varphi_{S}(0)\rangle = \lambda^{-1/2} \begin{pmatrix} \alpha \\ 1-\alpha \end{pmatrix} \Rightarrow \rho_{S}(0) = \lambda^{-1} \begin{pmatrix} \alpha^{2} & \alpha(1-\alpha) \\ \alpha(1-\alpha) & (1-\alpha)^{2} \end{pmatrix}$$

with normalization factor  $\lambda = \alpha^2 + (1 - \alpha)^2$ .

While the master equation became computationally very cheap due to the small dimension of the OQS, the effort in the DMRG computation is still potentially high because the full bath dynamics are computed, depending on the simulational parameters. This of course comes with the benefit of numerical precision and as exact solutions as desired for any coupling scale.

# 6.5 NUMERICAL RESULTS

We now turn to numerical results gained via the various methods introduced in the preceding sections. To this extend, we will demonstrate the dephasing for a  $\langle \sigma_x \rangle$ -excited initial state as predicted by the analytic computation 6.7 and compare it to the solution of the ME given by 6.13. The simulation employs the parameters

$$\omega_{c} = 0.3 \text{ eV} \quad \omega_{cut} = 0.6 \text{ eV} \qquad s = 1 \quad \omega_{S} = 0.3 \text{ eV} \quad (6.16)$$
  
 $\Delta = 0 \text{ eV} \qquad \beta = 10 \text{ eV}^{-1}$ 

and yields the results shown in fig. 6.2. The time evolution of the spin excitation takes the expected form: Oscillating with the two-level system frequency  $\omega_S$ , it decays with a coupling-dependent rate which is proportional to  $\alpha$  via  $\mathcal{J}$  as can be read off of 6.7. The deviation of the weak-coupling nMME solution without secular approximation from the exact solution is shown in fig. 6.2b) in form of the relative difference

$$\delta(\tau) = \left| \frac{\langle \sigma_{x,exact} \rangle (\tau) - \langle \sigma_{x,nMME} \rangle (\tau)}{\langle \sigma_{x,exact} \rangle (\tau)} \right|$$
(6.17)

and it can indeed be observed to grow with the coupling strength  $\alpha$ . This dependency is non-linear as expected due to our approximation up to quadratic order in  $\alpha$ . It should be noted, that the simulational parameter dt, which is not a physical quantity, has a major influence on the precision of the ME results and that it has to be chosen as



Figure 6.2: (*a*) Dephasing in the spin-boson model as predicted by the analytic solution. (*b*) Numerically computed *relative* difference between the weak-coupling ME and the exact solution.

Parameters are given in 6.16 and the continuous environment model 6.7 and dt = 5 keV<sup>-1</sup> are used for these computations,  $\alpha$  is given in eV.

a compromise between accurate results and limited computational effort. The presented results employ  $dt = 5 \text{ keV}^{-1}$  leaving us with a reasonably simple computation and properly precise results at the same time.<sup>7</sup> Investigating the dependence on dt in fig. D.4 in appendix D, we can state that for relevant regimes  $dt \in [0.001, 0.15]$  the relative error approaches a rule max  $\frac{\Delta \langle \sigma_x \rangle}{\langle \sigma_x \rangle} = m \cdot dt$  for bigger dt but for small time stepsizes, an error larger than this can be observed. This can be interpreted as a linear influence of dt relevant for bigger time increments which is superseded by a non-linear behaviour for small dt, leading to a non-vanishing error towards arbitrarily small stepsizes. This residual error is due to the approximations performed in the ME. We then can turn to the numerically exact simulation of the pure dephasing model, employing a DMRG analysis with the same parameters.<sup>8</sup> The corresponding results are displayed in fig. 6.3 where we see the absolute deviation between the simulation and the analytic solution. For small local bath dimensions mbath we see rather big errors on  $\langle \sigma_{\mathbf{x}} \rangle$  but they can be reduced to properly small regimes by increasing this purely simulational parameter. It is clear by our choice of the initial bath state  $\rho_B^\beta$  that the necessary truncation dimension of the bath depends on  $\beta$  and the amount of energy transferred into the bath by the OQS because the truncation neglects high-excitation states of the bath modes which are only relevant for small temperatures, that is big  $\beta$ , and for high energy transitions via interaction with the OQS. The influence of  $m_{bath}$  on the results is astonishingly big and will therefore be important in the upcoming analysis of the full system. We see an inverted dependence of the error on the coupling parameter  $\alpha$ , i. e. the stronger the coupling the smaller deviations are found. A

<sup>7</sup> Please note, that the overall scale of the deviations between the nMME and the exact result is fairly small.

<sup>8</sup> but a finite bath size L, of course

review of the dephasing dynamics shows that this is only due to the faster decay of  $\langle \sigma_{\chi} \rangle$  itself for bigger  $\alpha$ , which imposes a small deviation  $\Delta \langle \sigma_x \rangle$  given a constant *relative* error. However, as can be seen in fig. 6.3, for DMRG simulations it is the *absolute* value (or its periodic maximum) that is constant yielding strongly increased relative errors for  $\langle \sigma_{\chi} \rangle$  as it decays to 0. Nonetheless, the fact that we can reduce the error of the DMRG results by increasing the size of the simulated system assures us that the implementation works and matches the expected behaviour of a truncation-based approximation, and the constant absolute deviation is in agreement with this expectation as well. The time step size for DMRG was chosen bigger than for the ME in order to keep the computational effort in bounds and because its influence on the DMRG results has been observed to be neglegible. Again, it should be emphasized that the main purpose of figs. 6.2b) & 6.3 is not the direct comparison between the methods but the individual evaluation of their quality and sensitivity to simulational parameters. When comparing both please note that the shown quantities differ as fig. 6.2b) displays relative and fig. 6.3 shows absolute deviations from the corresponding analytic solution and different scales are used.



Figure 6.3: Numerical simulation of the pure-dephasing model including the bath using DMRG with different local bath dimensions  $m_{bath} = 5$ , 10 and 20 for the dotted, dashed and solid lines, respectively. The parameters are as in fig. 6.2 but we used  $dt = 0.05 \text{ eV}^{-1}$  and the absolute rather than the relative deviation from the analytic solution is shown. Furthermore, as DMRG is not treating an infinite system, we turned to the finite size L = 10 for both, the numerical simulation and the analytic solution 6.6. (Please note the logarithmic scale.)

We thus first can use the analytic solution to look at the influence of  $\mathcal{J}$  (section 6.6) and then can proceed to treat the spin-boson model

without analytic solution, that is for  $\Delta \neq 0$  (section 6.7), and the more complex full system (chapter 7).

# 6.6 STRUCTURED SPECTRAL DENSITIES - POKING THE DYNAMICS



Figure 6.4: (*a*) Spectral densities with peaks of Rhodamine 800 added (c.f. appendix A). Different numbers of peaks and different FWHM 2Γ were used.

(*b*) Resulting decay modulation in the dynamics of the pure dephasing model as computed by 6.7.

In order to give a qualitative insight into the influence of characteristic peaks in  $\mathcal{J}$  as introduced in appendix A, we will use the exact dephasing result and plug in a structured spectral density into 6.7. As a result the decay of the amplitude,  $exp[-\Gamma_b(t)t]$ , is shown in fig. 6.4 for a different number of selected peaks and Half Width at Half Maximum (HWHM)  $\Gamma$ . For this analysis, the peaks of Rhodamine 800 with properties taken from [12] are simply added to a smooth background.<sup>9</sup>

We observe an increased dephasing rate overall, which is clear by the fact that we increased the overall coupling. More interestingly, the rate is modulated with oscillations corresponding to the characteristic frequencies of the peaks. This means that for special relations between the two-level system frequency  $\omega_s$  and a single characteristic line  $\Omega$  in the bath the dynamics can be damped stronger or less strong. The choice of  $\omega_s = \Omega$ , for example, leads to an increased damping of the minima and a decreased damping of the maxima of  $\langle \sigma_z \rangle$  whereas  $\omega_s = \Omega/2$  yields bigger amplitudes for the minima. When testing these analytical insights in the system, the smooth background disturbs the clear differentiation of the cases and therefore we beforehand want to change our method slightly: For every peak added to the

<sup>9</sup> Please note that this changes the peak amplitude even though the experimentally measured values naturally include the background. We neglect this fact for this purely qualitative analysis.

spectral density, we rescale the smooth background  $\mathcal{J}_{BG}$  with a factor  $\kappa$  such that

$$\int_{0}^{\infty} d\omega \, \kappa \mathcal{J}_{BG}(\omega) + \mathcal{J}_{L}(\omega) = \int_{0}^{\infty} d\omega \, \mathcal{J}_{BG}(\omega). \tag{6.18}$$

This means that adding peaks changes the shape of the spectral density in dependence on the number and width of the peaks but preserves the overall coupling and keeps the density ohmic because of the linear low-energy modification of the peaks (see appendix A). With this modified strategy, we can investigate the influence of the peaks independently of the overall coupling  $\int_0^\infty d\omega \ \mathcal{J}(\omega)$ . This is in accordance with experimental procedures in vibrational specroscopy where the focus lies on the characterstic peaks and the background influence is of lower importance. The corresponding decay modulations  $e^{-\Gamma_b(t)t}$  and the results for  $\langle \sigma_x \rangle(t)$  are shown in fig. 6.5. We see a fairly reduced



Figure 6.5: Pure dephasing dynamics for a spectral density with a single peak, renormalized via 6.18. When tuning the spin frequency to the decay in (*a*), which is is reduced significantly for long times even though the overall coupling is fixed, we can modify the amplitude in the  $\langle \sigma_x \rangle$  (t) excitation for the first extrema in (*b*). Please note the different time ranges.

damping prefactor of the  $\langle \sigma_x \rangle$  (t) oscillations for the peaked spectral densities in fig. 6.5a), even though the coupling is renormalized to a constant overall coupling strength. This shows that the characteristic lines are less effective at damping the dynamics, i. e. they provide a less effective dissipative behaviour. Due to the temperature influence in  $\Gamma_b(t)$  we can understand this phenomenon: The contributing factor  $\left(\frac{\beta\omega}{2}\right)$  filters out low-energy contributions and therefore the low-energy behaviour is most important for the observed dynamics. Interestingly, this fits to the common understanding of Markovian dynamics, even though the above results are exact.

Subsequently, we want to check the estimated behaviour for specific choices of the spin frequency, which merely amounts to *selecting* the times t for which the damping is explicitly stronger or weaker than for the background alone by synchronizing them with the maxima in

magnitude of the factor  $\cos(\omega_S t)$ .<sup>10</sup> The results of tuning  $\omega_S$  to  $\Omega_1$  an  $\Omega_1/2$ , respectively, are shown in fig. 6.5b) and indeed confirm the desired behaviour for the first extrema of the dephasing dynamics: For  $\omega_S = \Omega_1$  we see a stronger damping of the first two minima, compared to the less damped amplitude of the first maximum. For  $\omega_S = \Omega_1/2$ , the first minimum lies at the first maximum of the previous tuning, such that we see a weakly damped first minimum. These were exactly the expectations. It should be noted, that this can be done for single extrema primarily and all further occurences of maximized or minimized damping are due to mutual periodicity of the decay and the oscillatory part in  $\langle \sigma_x \rangle$  (t).

Furthermore we want to emphasize, that even though this analysis is fairly straight forward, it can lead to interesting insights on the interplay between the OQS and the bath, especially for structured spectra. For future investigations it might be interesting to find special modifications of the spectral density which induce more complex or repeated structures in the system dynamics. This then could be exploited by using an OQS with more frequencies that then could be adapted to the specialized bath. However, we will leave this to future work and go on with an investigation on the role of the secular approximation.

## 6.7 THERMAL INFLUENCE ON THE SECULAR APPROXIMATION

In this section we want to analyze the influene of the secular approximation in the spin-boson-model as we have the possibility to gain analytic insights on this to some extend. The nMME with and without the secular approximation was seen to give very different results when treating the thermal stationarity in section 4.4. While the secularly approximated equation predicts a stationary thermal state, a movement away from this state is seen for the other ME and confirmed by the numerical simulation with the DMRG setup. As we saw the MME to coincide well with the non-Markovian equations, we will employ the Markov approximation, making use of analytic insights first shown in [34]. This enables us to evaluate our implementations with yet another benchmark and at the same time gain insights on the secular approximation.

We start out by trying to solve the ME analytically for the general spinboson model. For this we follow the approach of [34], which employs a rotation of the OQS subspace Hamiltonian and a corresponding change

<sup>10</sup> This is the only contribution for  $\rho_S^{+-}(0)\in\mathbb{R}.$ 

of what is understood as interaction picture. Due to the specific choice of this rotation, this diagonalizes  $H_S$ ,

$$\widetilde{H}_{S} = U^{\dagger} \left( \frac{\omega_{S}}{2} \sigma_{z} + \frac{\Delta}{2} \sigma_{x} \right) U = \frac{\eta}{2} \sigma_{z} \text{ for } U = e^{-i\vartheta \sigma_{y}/2}$$
  
with  $\eta = \sqrt{\omega_{S}^{2} + \Delta^{2}}$  and  $\vartheta = \begin{cases} \pi/2 & \text{for } \omega_{S} = 0\\ \arctan \frac{\Delta}{\omega_{S}} & \text{for } \omega_{S} \neq 0 \end{cases}$ 

making the computation of the master equation easier. Carrying out the derivation as in chapter 4 and employing the spectral decomposition, we arrive at the following for the *Schrödinger picture* master equation in the Markovian approximation:

$$\begin{split} \widetilde{\rho_{S}}(t) &= -i\frac{\eta}{2} \left[ \sigma_{z}, \widetilde{\rho_{S}}(t) \right] + \sum_{\omega, \omega'} \left( \kappa(\omega') \left[ \mathsf{P}(\omega') \widetilde{\rho_{S}}(t), \mathsf{P}(\omega) \right] + \text{h.c.} \right) (6.19) \\ \text{with} \quad \kappa(\omega') &= \int_{0}^{\infty} d\tau \; e^{i\omega'\tau} c(\tau) \;, \; \widetilde{H_{I}}(t) = \sum_{\omega} \mathsf{P}(\omega) e^{-i\omega t}, \end{split}$$

the sum running over  $\{-\eta, 0, \eta\}$  and where the tilde denotes the rotated frame throughout. For our system the spectral operators are

$$P(0) = \frac{\omega_S}{\eta} \sigma_z$$
  $P(\pm \eta) = \frac{\Delta}{\eta} \sigma_{\mp}.$  (6.20)

The secular approximation, which is carried out in the interaction picture, yields an equation of reduced complexity due to the requirement  $\omega' = -\omega$  originating from the approximation procedure as described in section 4.3.<sup>11</sup>

$$\widetilde{\dot{\rho_{S}}}(t) = -i\frac{\eta}{2} \left[\sigma_{z}, \widetilde{\rho_{S}}(t)\right] + \sum_{\omega} \left(\kappa(-\omega)[P(-\omega)\widetilde{\rho_{S}}(t), P(\omega)] + h.c.\right) (6.21)$$

We now solve the above MMEs for the special case of  $\omega_S = 0$ , corresponding to the first case in [34] and enabling us to compare the results of the secular and the non-secular equation, and for the initial state  $\rho_S(0) = a|-\rangle\langle-|+(1-a)|+\rangle\langle+|$ . The spectral operators become P(0) = 0,  $P(\pm \eta) = \sigma_{\mp}$  and we have  $\vartheta = \pi/2$  as well as  $\eta = \Delta$ . Because of the special setup for  $\omega_S = 0$ , the basic interesting quantity we consider is  $\langle \sigma_z \rangle$  (t). From the componentwise treatment of 6.19 we obtain the solutions

$$\langle \sigma_z \rangle (t) = \langle \sigma_z \rangle (0) e^{-At} \left[ \cos (Bt) + \frac{A}{B} \sin (Bt) \right]$$
 (6.22)

and

$$\langle \sigma_z \rangle (t) = \langle \sigma_z \rangle (0) e^{-At} \cos(Ct)$$
 (6.23)

for the non-secular and the secular ME, respectively. We introduced the abbreviations

$$\begin{split} \mathsf{A} &= \mathfrak{Re}\{\kappa(\Delta) + \kappa(-\Delta)\} \\ \mathsf{B} &= \sqrt{\Delta^2 + 2\Delta}\mathfrak{Im}\{\kappa(\Delta) - \kappa(-\Delta)\} - \mathsf{A}^2 \\ \mathsf{C} &= \Delta + \mathfrak{Im}\{\kappa(\Delta) - \kappa(-\Delta)\} \end{split}$$

<sup>11</sup> As we follow the notation of Nazir [34] here, the condition  $\omega' = \omega$  becomes  $\omega' = -\omega$ .

and can write

$$\begin{split} A &= \int_{0}^{\infty} dt \, 2 \cos(\Delta t) \mathfrak{Re}\{c(t)\} \qquad A' = \int_{0}^{\infty} dt \, 2 \sin(\Delta t) \mathfrak{Re}\{c(t)\} \\ B &= \sqrt{\Delta^2 + 2\Delta A' - A^2} \qquad C = \Delta + A'. \end{split} \tag{6.24}$$

Let us first analyze the non-secular solution, which exhibits a transition between qualitatively different time evolutions [34]:

For  $\Delta^2 + 2\Delta A' \ge A^2$  we know B to be real and positive. This means, that the  $\langle \sigma_z \rangle$ -excitation decays in an oscillating manner, with amplitude decay  $e^{-At}$  and a weighted combination of a cosine and a sine wave. Because of the dependence of A and A' on the real part of the correlation function and the monotonous decrease relation between  $\beta$  and c(t), we see the above condition fulfilled if the temperature is properly *low*, corresponding to big values of  $\beta$  and therefore to smaller A and A'.

A different behaviour is seen in the case when  $\Delta^2 + 2\Delta A' < A^2$ . Here we find B to be purely imaginary, converting the oscillatory factors in 6.22 to real exponentials, of which one slows down the decay by a contribution  $e^{\Im m\{B\}t}$ . This case, demanding large A and A', corresponds to large temperatures. In summary, the case separation is

$$\Delta^{2} + 2\Delta A' \ge A^{2} \implies \text{Damped oscillation}$$
  
$$\Delta^{2} + 2\Delta A' < A^{2} \implies \text{Reduced exponential decay}$$

The corresponding temperature regimes and the transition between the cases can then be found numerically,<sup>12</sup> for now we just give exemplary time evolutions in fig. 6.6 (solid lines) with parameters

$$\omega_{c} = 0.3 \text{ eV} \quad \omega_{cut} = 0.6 \text{ eV} \quad s = 1 \quad \omega_{S} = 0 \text{ eV} \quad (6.25)$$
  
 $\Delta = 0.3 \text{ eV} \quad \alpha = 0.05 \text{ eV}$ 

As mentioned above, we also want to use the present system as a benchmark and therefore numerically evaluate the MME as well. As for the pure dephasing case treated above, we find excellent coincision and therefore refrain from displaying both the numeric result. Having understood the non-secular results we want to turn to the secular ME results in 6.23 and analyze them in a similar fashion. Due to the simpler form of C compared to B, we do not find different behaviour in dependence on the temperature but always obtain an exponentially decaying cosine wave. It is therefore clear, that for small temperatures, where A and A' are small, we can find coinciding results between the two ME solutions. Consequently we can state that the secular approximation only works for small temperatures, which is confirmed with the secular MME results shown in fig. 6.6 (dashed).

<sup>12</sup> For the parameters in 6.25 we obtain the huge transition temperature of  $T_{\tt crit}=24000^\circ K$ 



Figure 6.6: Time evolution of the  $\langle \sigma_z \rangle$ -excitation for three different temperatures exhibiting the three fundamentally different forms of dynamics derived here (Solid). Additionally the secularly approximated dynamics are displayed (Dashed), showing better coinciding results for small temperatures. The parameters are given in 6.25

Before moving on, we want to refine the understanding of the transition in the quality of the secular approximation. We start by noting that the condition  $\Delta^2 + 2\Delta A' \ge A^2$ , which discriminates the oscillatory and the monotonous scenarios in the non-secular dynamics, leads to the statement  $A < \Delta$  when assuming  $A \sim A'$ . Guided by this, we look at the limit  $A \ll \Delta$ , in expectation of coinciding secular and non-secular dynamics, and by comparing orders and relations between the used quantities, we can write:

$$\Delta \gg \mathfrak{Re}\{c(t)\} \Rightarrow \omega' - \omega \gg \Gamma \Rightarrow (\omega' - \omega)\tau \gg 1.$$

where we wrote  $\Gamma$  for the decay rate induced by the bath. The latter inequality is the condition of validity for the secular approximation as it is commonly known, showing that the secular approximation is self-consistent and explicitly demonstrating its connection to the temperature of the bath, which is incorporated in  $\Re \epsilon \{c(t)\}$ .

Outside of the special case  $\omega_S = 0$ , the non-secular ME is not solvable analytically and we therefore refrain from extending the analysis to that regime. However, we want to emphasize the insight we gained from the above work: The secular approximation changes the solution of the corresponding master equation in a temperature-dependent manner, always displaying damped oscillations for our case, and we therefore have to go to a proper temperature regime if we want to gain qualitatively coinciding results or want to rely on the secular MME alone, for example when requiring a master equation in Lindblad form. In this chapter we now consider the full system as introduced in 2.5 and analyze its dynamics. We will make use of the insights gained throughout the previous chapters, enabling us to choose proper simulation parameters and the correct methods in order to arrive at meaningful results.

Please note, that we will restrict ourselves to the case  $\Delta = 0$  in order to investigate the influence of the cavity on the dephasing of the spin. It should be noted that for more interesting thermalization dynamics of the cavity mode itself,  $\Delta \neq 0$  is expected to be essential. As we learned in the previous chapters, the energy exchange between the OQS and the bath is mediated via H<sub>CS</sub> alone if there is a spin-bath-coupling diagonal in the spin Hamitonian. It thus is clear, that the ultimate goal of finding whole parameter regimes in which the cavity thermalizes is not reached within this work but will have to be pursued in its final steps in upcoming projects.

## THE CAVITY DISTURBS PURE DEPHASING

We will look at the special case  $\Delta = 0$ , which we saw to exhibit special features in the spin-boson model, such as an analytic solution and a stationary energy of the two-level system. For the full system, the interaction Hamiltonian between the cavity mode and the spin, H<sub>CS</sub> is the only part of H<sub>S</sub> which allows for energy flow from the OQS to the bath and vice versa, because  $[\omega_S/2\sigma_z, H_I] = [\omega_C a^{\dagger} a, H_I] = 0$  but  $[H_{CS}, H_I] \neq 0$ . Therefore, the OQS will only change its energy if interactions between spin and cavity mode occur via H<sub>CS</sub>, enabling H<sub>I</sub> to act on the overall system energy E<sub>S</sub> =  $\langle H_S \rangle$ .

For  $\Delta = 0$ , we furthermore can show particle number conservation. To this end, we define the particle number as  $\mathcal{N} = a^{\dagger}a + \frac{\sigma_z + \mathbb{1}}{2}$ , that is the sum of the subsystem particle numbers w. r. t. their Hamiltonians, ignoring the interaction Hamiltonian  $H_{CS}$ . We then first compute

$$[\mathbb{N}, \mathbb{H}_{S}] = g\left([a^{\dagger}a, a^{\dagger}\sigma^{-} + a\sigma^{+}] + \frac{1}{2}[\sigma_{z}, a^{\dagger}\sigma^{-} + a\sigma^{+}]\right)$$

$$= a^{\dagger}\sigma^{-} - a\sigma^{+} - \frac{1}{2}(2a^{\dagger}\sigma^{-} - 2a\sigma^{+}) = 0$$

$$\Rightarrow V_{t}\mathbb{N} = \mathbb{N}$$

$$(7.1)$$

and subsequently evaluate the time evolution of N with the non-Markovian master equation 4.12:

$$\langle \hat{\mathcal{N}} \rangle (t) = 2 \mathfrak{Re} \{ \operatorname{tr} \{ V_t \mathcal{N} [ V_t \mathsf{K}(t) \ \rho_S(t), V_t \sigma_z] \} \}$$
  
= 2 \text{Re} \{ \operatorname{tr} \{ [ V\_t \sigma\_z, \mathcal{N}] V\_t \mathsf{K}(t) \ \rho\_S(t) \} \}   
= 0 (7.2)

where the last equality is due to  $[V_t \sigma_z, \mathcal{N}] = V_t[\sigma_z, \mathcal{N}] = 0$  which holds because of 7.1 and  $[\sigma_z, \mathcal{N}] = 0$ . We thus have particle number conservation for the present system.

The clear separation between the open system dynamics and the bath interaction, which we explained above, allows us to artificially construct states which are stationary in an exact treatment. For this, we observe that in order to yield cavity-spin interactions, it must be possible to create or annihilate an excitation in the cavity and to do the respective opposite in the two-level system. By initializing the system in the state  $\rho_S(0) = |0\rangle\langle 0| \otimes |-\rangle\langle -|$ , i. e. the product state of the subsystem ground states, we can prevent these transitions from happening and therefore get a stationary state:

$$\begin{split} \dot{\rho} &= -i \left[ H, \rho(0) \right] = -i \left[ H_S, \rho_S(0) \right] \otimes \rho_B^\beta - i \rho_S(0) \otimes \left[ H_B, \rho_B^\beta \right] \\ &\quad -i |0\rangle \langle 0| \otimes \left[ H_I, |-\rangle \langle -| \otimes \rho_B^\beta \right] \\ &= -i (E_0 - E_0) \rho(0) - i (E_B^\beta - E_B^\beta) \rho(0) \\ &\quad + \frac{i}{2} (\omega_S - \omega_S) \rho_S(0) \otimes (\mathcal{B} \rho_B^\beta) + \frac{i \omega_S}{2} \rho_S(0) \otimes \left[ \mathcal{B}, \rho_B^\beta \right] \\ \dot{\rho_S} &= \frac{i \omega_S}{2} \rho_S(0) \cdot tr \left\{ \mathcal{B} \rho_B^\beta - \rho_B^\beta \mathcal{B} \right\} = 0 \end{split}$$
(7.3)

Here we used the explicit form of the initial state, which is an eigen state of H<sub>S</sub> and H<sub>B</sub> with energies E<sub>0</sub> and E<sup>β</sup><sub>B</sub>, respectively. The periodicity of the trace then yields a vanishing rate of change for the OQS density matrix overall. Due to the finite number of bound states in the cavity mode within our numerical simulations, we actually can design a state with highest excitations w.r.t. the subspace Hamiltonians H<sub>cvty</sub> and H<sub>spin</sub> which also fulfills the above stationarity, namely  $\rho_S^{max} = |m_{cvty} - 1\rangle \langle m_{cvty} - 1| \otimes |+\rangle \langle +|$ . However, this is not a very reasonable initial state by means of physicality, because it exploits the truncation of the harmonic mode, which itself is made under the condition that it does not severely restrict the dynamics and only truncates unimportant transitions in the system. This condition clearly would be violated for  $\rho_S^{max}$ .

The numerical simulation with both of the above initial states correctly reproduces the stationary behaviour.<sup>1</sup>

Now we can turn to analyzing the system dynamics for more interesting initial states and investigate whether the system or the cavity

<sup>1</sup> We refrain from showing the plots here as they simply display constants.
mode alone thermalize. To this end, we start in the ground state of the cavity but initialize the spin in a mixed state, such that

$$\rho_{S}(0) = |0\rangle\langle 0| \otimes |*\rangle\langle *| \quad \text{with} \quad |*\rangle = \sqrt{2}^{-1}(|-\rangle + |+\rangle). \tag{7.4}$$

We will employ the following parameters for the ME computation:

$$\omega_{c} = 0.3 \text{ eV} \quad \omega_{cut} = 0.6 \text{ eV} \quad s = 1 \quad \beta \in \{1, 100\} \text{ eV}^{-1} \quad (7.5)$$
  
 $\omega_{S} = 0.3 \text{ eV} \quad \Delta = 0 \text{ eV} \quad \omega_{C} = 0.3 \text{ eV} \quad g = 0.1 \text{ eV} \quad m_{cvty} \stackrel{2}{=} 4$ 

This enables us to compare the system dynamics for different temperatures of the bath, which is taken to be infinitely big, i.e. the exact correlation function is used here. Furthermore, we will choose the nMME without secular approximation as explained in section 4.4, yielding the OQS behaviour displayed in fig. 7.1 for the different temperatures. We start by looking at the energy of the open system  $\langle H_S \rangle$ 



Figure 7.1: Dynamical behaviour of the full system for the parameters in 7.5 with high ( $\beta = 1 \text{ eV}^{-1}$ , orange) and lower ( $\beta = 100 \text{ eV}^{-1}$ , red) temperatures. We look at the OQS energy and the  $\langle \sigma_x \rangle$  excitation in (*a*) and at the population and coherences of the cavity in (*b*).

in fig. 7.1a). For the higher temperature case, the OQS roughly stays at its initial energy value whereas the bath at lower temperature absorbs energy contained in the cavity and the spin, bringing them to the ground state energy of  $H_{cvty} + H_{spin}$ . The spin excitation dynamics depend heavily on the bath temperature and qualitatively different behaviour occurs: While the low-temperature environment only induces a mediocre decay of the oscillations and then even allows for oscillations with growing amplitude, the hot bath quickly damps them towards the equilibrium value 0. Correspondingly, a similar behaviour is seen for the coherences of the cavity mode,  $\langle a^{\dagger} + a \rangle$  displayed in fig. 7.1b). This means that the hot bath suppresses interaction of the two-level system and the harmonic mode, whereas the open system in the cold lower-temperature environment enters a pseudo-stationary state with ongoing excitation exchange of coherences, even when the

<sup>2</sup> For the given initial state, this truncation of the harmonic cavity mode has been shown to be sufficient.

occupations of both subsystems reached equilibrium already. Finally, we look at the occupation of the cavity,  $\langle a^{\dagger}a \rangle$ , which converges with a temperature dependent decay towards the same final value for all temperatures we investigated<sup>3</sup> and is constrained by the particle number preservation shown above. The occupation number of the spin is the corresponding complement and therefore not shown here. An analysis of the trace distance between the thermal state and the time evolved states for the cavity and the entire OQS, respectively, showed that the observed convergence towards a (pseudo-)stationary state does not show thermalization but that a different state is attained. This can be understood in the light of the particle number conservation because the fixed particle number from our initial state is  $\mathcal{N} = \frac{1}{2}$  and the thermal states contain  $\mathcal{N}(\beta = 1 \text{ eV}^{-1}) = 1.06$  and  $\mathcal{N}(\beta = \overline{100} \text{ eV}^{-1}) = 0$ particles, respectively. Therefore at least the initial particle number would need to be tuned to its thermal equivalent in order to not strictly prevent thermalization.

For future work it will be interesting to consider the system in a setting without particle conservation, that is for  $\Delta \neq 0$ . We then expect richer dynamics and the possibility to thermalize the OQS. Furthermore, the thermalization of the cavity alone has been shown for a weak cavity mode to spin coupling [28] and we will be able to test these statements with the help of our DMRG implementation.

<sup>3</sup> Including multiple more in the range  $\beta \in [0.1 \ eV^{-1}, 100 \ eV^{-1}]$  than the ones shown in fig. 7.1

### Part III

# APPENDIX

We introduce typical spectral densities that are used throughout the project and that resemble a realistic choice for the dye molecule in the cavity, namely Rhodamine 800, in chapter A. On a rather technical level that would be distracting for the main text we introduce orthogonal polynomials in chapter B as a preparation to Gaussian quadrature rules and the optimized bath discretization strategy in section 3.2. In chapter C we discuss the physicality of the nMME or - to be precise - its violation, complementing the corresponding sections 4.2 and 4.4.



Throughout the thesis, we introduce the bath spectral density  $\mathcal{J}$  as a helpful quantity for the description of physical systems, which provides connections to other theories and measurements. Here we want to briefly discuss the used examples of spectral densities.

We start with the Caldeira-Leggett spectral density, which is given by

$$\mathcal{J}(\omega) = \alpha \left(\frac{\omega}{\omega_c}\right)^s e^{-\omega/\omega_c}, \ \omega > 0$$

with normalization constant or coupling parameter  $\alpha$ , ohmicity s and critical frequency  $\omega_c$ . For low frequencies, there is a monomial behaviour with power s and the cases s < 1, s > 1 and s = 1 are called sub-, super- and ohmic. This growth is suppressed by the exponential cutoff for higher frequencies. This allows us to consider an arbitrary frequency band - including the semi-infinite interval  $[0, \infty)$ - as it bounds  $\mathcal{J}$ , therefore giving it a finite norm and in particular assuring that  $\mathcal{J}$  generates a continuous measure such that the optimized frequency sampling algorithm can be used (c. f. appendix B). The second possibility to guarantee these properties is to include a step-shaped cutoff in the spectral density, which we will do in most cases. For consistency reasons with the infinite range case and with experimentally obtained densities (see below), we will nonetheless keep the exponential term in the case of a finite support of  $\mathcal{J}$ , giving us our standard spectral density as

Caldeira-  
Leggett 
$$\mathcal{J}(\omega) = \alpha \left(\frac{\omega}{\omega_c}\right)^s e^{-\omega/\omega_c} \Theta(\omega_{cut} - \omega), \quad \omega > 0 \text{ (A.1)}$$

with the Heaviside step-function  $\Theta$  and step cutoff frequency  $\omega_{cut}$ .<sup>1</sup> The Caldeira-Leggett model is empirically motivated and one of the standard settings for  $\mathcal{J}$ , being widely used in purely theoretic considerations [38] and investigations towards applications, e.g. in quantum chemistry [33, 43]

The second example we want to present here is the spectral density of the molecule Rhodamine 800. It has been measured reliably and on a detailed level with modern vibrational spectroscopy methods [12] and was used in theoretical studies as an example for molecules in interaction with an electromagnetic mode in a cavity [35, 36], just like

<sup>1</sup> We will refer to this version of the spectral density as Caldeira-Leggett shape whereas the first expression without step cutoff is the original but unused version.



Figure A.1: Spectral densities for the bosonic bath. Examples for J of Caldeira-Leggett type (left) and the measured spectrum of Rhodamine 800 including a smooth background (right); Peak data is taken from [12].

our system.

The spectrum of Rhodamine 800 consists of 16 characteristic peaks, which are described by their frequency v and reorganisation energy  $\lambda$ . With a FWHM 2 $\Gamma$  depending on the temperature, the peaks are modelled as usual using a Lorentzian for each peak, given by

$$\mathcal{J}_L(\omega) = \lambda \frac{\Gamma^2}{(\omega - \nu)^2 + \Gamma^2}$$

which is normalized to  $\lambda\Gamma\pi$  and has the maximum  $(\nu, \lambda)$ . Note that the sum of these peaks will give us a nonvanishing coupling for  $\omega = 0$ , which yields problems for the continuous description we use in some parts of our work. We therefore modify the Lorentzians by replacing the low-frequency tail of  $\mathcal{J}_L$  by a linear relation, tailored to give a continuous and continuously differentiable function with  $\mathcal{J}(\omega) = 0$ . It is uniquely determined and reads

$$\mathcal{J}_{\text{peak}}(\omega) = \begin{cases} \eta \omega & \text{for } \omega \leq \omega^* \\ \mathcal{J}_{L}(\omega) & \text{for } \omega > \omega^* \end{cases}$$
(A.2)

with the  $\omega^*$  chosen such that the continuous slope condition can be fulfilled and  $\eta = \mathcal{J}_L'(\omega^*)$ .

In addition to the peaks, the spectrum contains a smooth background which we take to be of the above Caldeira-Leggett type, such that the characteristic peaks are simply an addition to our standard spectral density. We show examples of the spectral density in fig. A.1.

## ORTHOGONAL POLYNOMIALS

For the procedure of Gaussian quadrature, which is used in the optimized frequency sampling algorithm for the bath discretization, we require some basics about orthogonal polynomials. We mainly take these from [40].

We start with a weight function *w* which fulfils the following three conditions:

- 1. *w* is defined on the (possibly infinite) interval [a, b]and  $w(x) \ge 0 \forall x \in [a, b]$
- 2. For all  $k \in \mathbb{N}_0$ , the moment  $\mu_k = \int_a^b dx \; x^k w(x)$  is well-defined and finite.
- 3. For all polynomials q with  $q(x) \ge 0 \ \forall x \in [a, b]$  it holds that  $\int_a^b dx \ w(x)q(x) = 0 \Rightarrow q(x) \equiv 0$

As mentioned in [40], an exemplary case for which these requirements are satisfied is given when *w* is continuous on [a, b],  $w(x) > 0 \ \forall x \in$ [a, b] and |a|,|b| <  $\infty$ . In most cases throughout the thesis, we will consider weight functions of this type and if not, *w* still will be a positive function and an exponential cutoff enforces property 2 to hold, while the last point above is assured by  $\int_a^b dx w(x) > 0$ . For the quadrature rule, the following statement is important, enabling us to use the procedure on any weight function in the above sense:

For all weight functions w with the properties above there exists a unique set of monic polynomials  $\{p_j\}_j$  which are orthogonal w.r.t. the scalar product  $\langle f, g \rangle = \int_a^b dx w(x) f(x) g(x)$ .

Monic polynomials are those of the form

$$p(x) = x^{\deg p} + a_1 x^{\deg p-1} + \dots + a_{\deg p}$$
(B.1)

and we note that orthogonality is invariant under scalar multiplication, such that there is a unique second set of polynomials  $\{\tilde{p}_j\}_j$  when requiring ortho*norm*ality, i. e.  $\langle \tilde{p}_i, \tilde{p}_j \rangle = \delta_{ij}$ .

In addition to the existence statement, there is an explicit recursion

relation to generate the coefficients for  $p_j$ , such that knowing *w* is sufficient to find  $\{p_j\}_j$ :

$$\begin{array}{rcl} p_{-1}(x) &=& 0 & p_{0}(x) = 1 \\ p_{j+1}(x) &=& (x - \alpha_{j+1})p_{j}(x) - \beta_{j+1}^{2}p_{j-1}(x) \ \forall j \ge 0 & (B.2) \\ & \mbox{ with } & \alpha_{j+1} = \frac{\langle xp_{j}, p_{j} \rangle}{\langle p_{j}, p_{j} \rangle} \\ & \mbox{ and } & \beta_{j+1}^{2} = \begin{cases} 1 & \mbox{ for } j = 0 \\ \langle p_{j}, p_{j} \rangle / \langle p_{j-1}, p_{j-1} \rangle & \mbox{ for } j > 0 \end{cases} \end{array}$$

It is the universality of this recursion relation for all weight functions *w* which enables us to implement the Gaussian quadrature conveniently and efficiently.

Furthermore, one can show that the j roots of  $p_j$  are simple, i. e. pairwise distinct, and lie in the open interval (a, b). This assures the bath frequencies that are computed by the optimized sampling algorithm to be real, distinct and to lie in the frequency band on which the bath spectral density is defined.

As mentioned in the main text, the Gaussian quadrature is of exactness degree 2L - 1, meaning that integrals of the form  $\int_{a}^{b} dx w(x)p(x)$  are reproduced *exactly* by a weighted sum of p at L points for degrees of p up to 2L - 1, i.e.

$$\int_{a}^{b} dx \ w(x)p(x) - \sum_{i=1}^{L} W_{i}p(x_{i}) = 0 \ \forall p: deg \ p < 2L. \tag{B.3}$$

Here  $\{x_i\}_{1 \le i \le L}$  are the roots of  $p_L$  and the  $\{W_i\}$  can be computed explicitly as the solutions to the system

$$\sum_{i=1}^{L} p_k(x_i) W_i = \begin{cases} \langle p_0, p_0 \rangle & \text{for } k = 0\\ 0 & \text{for } 1 \leq k \leq L - 1 \end{cases}$$
(B.4)

which are uniquely determined because all roots are distinct. One can relate the first equation in this system of equations to the constraint with the norm of the spectral density 3.5 because  $p_0 \propto x^0$  and therefore

$$\sum_{i=1}^{L} W_i = \int_{a}^{b} dx \ w(x).$$
 (B.5)

We now turn to the computational aspects of the orthogonal polynomial strategy. As the quadrature we are aiming at exactly corresponds to B.3, we want to sample the bath frequencies at the roots of  $p_L$ , requiring us to implement a stable routine that finds these roots as well as the solutions  $W_i$  to the system of equations B.4. This is done for example in [18] and [37] and our implementation follows these routines.

## VIOLATION OF PHYSICALITY WITHOUT MARKOV APPROXIMATION

In this chapter we are going to briefly discuss the appearance of unphysical results when considering the non-Markovian master equation. The purpose of doing so is not to give a full analysis of parameter spaces regarding the failure of the method but to demonstrate that in principle, unphysical results can be generated when the Markov approximation is not employed.

For the Born-Markov master equation, which can be brought into Lindblad form, Lindblad himself showed complete positivity and that the time evolution is preserving the trace of  $\rho_S$  [31], which later was extended to systems with positive time-dependent decoherence rates [8, 46].<sup>1</sup>. Furthermore, the Markovian master equation can be shown to have the thermal system state (with the temperature of the bath) as a stationary solution, that is

$$\rho_{\rm S}^{\rm (th)} = \mathcal{Z}_{\rm S}^{-1} e^{-\beta H_{\rm S}} \qquad \dot{\rho_{\rm S}}^{\rm (th)}(t) = 0$$
 (C.1)

which is not true in general for the non-Markovian description (see section 4.4).

For systems with at least one rate which is not positive for all times, complete positivity is violated and there might appear unphysical results throughout the time evolution of the system [7, 8]. The conclusion is then that the setting of the Born-approximated master equation fails to describe the physical system and instead generates a pathologic unphysical system. It then also becomes clear that invoking the Markov approximation - despite the fact that the system itself can be shown to be non-Markovian - leads to a physical description if and only if the resulting time-independent rates are positive. This amounts to the condition of the partially negative rates to compensate the negative values by positive parts when integrated up to infinite times.

Combined, these results are rather remarkable: Skipping an assumption on our system and refraining from using the corresponding approximation, our description of the physical system gets distorted significantly in the case of decoherence rates which are not positive at all times. Performing the additional approximation, those problems

<sup>1</sup> These systems are referred to as time-dependent Markovian which might lead to confusion as intuitively such systems could be considered Markovian which are *described* in a Markovian way, i. e. with the Markov approximation. We will consider *Markovianity* as a system property and refer to the approximative description as *Markovian master equation*; A measure of Markovianity is introduced in [8], an extended overview is given in [9]

are resolved and the effective description via the master equation is valid for a physical system (although one expects major deviations from the real behaviour of the treated system). A similar phenomenon has been found for the Born approximation, which we also use in our work, showing that the Born approximation seems to level out flaws introduced into the theory by the other approximation schemes [51].

# D

## SUPPLEMENTARY FIGURES

Here we show some additional figures, which contain insightful information and are mentioned throughout the thesis. They were decided to be appended in order to not tear the main text because of too many pictures.



Figure D.1: Revival time  $\tau_{rev}$  for parameters as in fig. 3.2 but for linearly sampled bath frequencies. The standard deviation displayed on top is significantly reduced corresponding to an even smaller temperature dependence in comparison with the optimized sampling method. See fig. D.2 for a comparison between the results of the two sampling methods.



Figure D.2: Difference of the revival times for both sampling methods, corresponding to fig. 3.2 & D.1. As can also be seen by the scale, the linear sampling always yields bigger revival times. Note that the reduction to 0 for big bath sizes L is artificial due to the 300  $eV^{-1}$  bound for  $\tau_{rev}$ .



Figure D.3: Factor between the average deviation for both sampling methods, corresponding to fig. 3.4 & 3.5. As can also be seen by the scale, the linear sampling always yields much bigger deviations, at least by a factor of 10.



Figure D.4: Maximal relative deviation of the ME solution for the spin expectation value  $\langle \sigma_x \rangle$  (corresponding to the maxima in fig. 6.2) for the same couplings as in fig. 6.2 and various time stepsizes dt. The lines are adapted to the last three data points, please note that due to the logarithmic scale all linear laws  $y = m \cdot x$  are displayed as parallel lines with differing offsets:  $\log y = \log m + \log x$ .

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## ERKLÄRUNG / DECLARATION

## Selbständigkeitserklärung

Hiermit erkläre ich, die vorliegende Arbeit selbstständig verfasst und keine anderen als die genannten Quellen und Hilfsmittel verwendet zu haben.

Diese Arbeit wurde nicht zuvor publiziert oder als Abschlussarbeit andernorts vorgelegt.

### Declaration of Authorship

I confirm that this Master's thesis is my own work and I have documented all sources and material used.

This thesis was not previously presented to another examination board and has not been published.

München, November 2018

David Wierichs