Reduced Operator Approximation for modelling open quantum systems

Agnieszka Werpachowska*

Department of Physics and Astronomy, University College London,
Gower Street, London WC1E 6BT, United Kingdom

We present the Reduced Operator Approximation: a simple, physically transparent and computationally efficient method of modelling open quantum systems. It employs the Heisenberg picture of the quantum dynamics, which allows us to focus on the system degrees of freedom in a natural and easy way. We describe different variants of the method, low- and high-order (including the interaction operators), defining them for either general quantum harmonic oscillators baths or specialising them for independent baths with Lorentzian spectral densities. They are applied to different systems (coupled to different baths with different strengths) and compared with the exact pseudomode and the popular quantum state diffusion method.

I. INTRODUCTION

The beginning of twentieth century launched a series of major paradigm shifts which heralded the era of modern physics. It will perhaps be surprising to the modern reader that in the advent of the revolutionary Einsteinian theory of relativity, Maxwell and Boltzmann's kinetic theory and Planck's hypothesis of quanta, the scientific world was not convinced of the fact that matter is grainy and cannot be continuously divided infinitely [1]. The seed of doubt was planted by the renowned Scottish botanist, Robert Brown, who noticed in 1827 that pollen in water suspension which he examined under his microscope displayed a very rapid, irregular, zigzag motion. The mystery of the "vital force" driving the Brownian motions remained unsolved for nearly 80 years, evading the pincer of conventional physics. The answer came from Einstein and Smoluchowski, who showed how the behaviour of mechanical objects is driven by the statistical properties of thermal noise, postulating the existence of molecules in the fluid and linking the diffusion strength of their motion to the friction acting on a body moving in the fluid [2, 3]. The explanation of Brown's experiments, being at the same time a major diversion from the "continuous" Newtonian dynamics forming the core of the contemporary physics, opened a whole new avenue of research into the behaviour of systems influenced with random noise, resulting in such fundamental discoveries as the fluctuation-dissipation theorem [4, 5]. Since that time, dissipation has been shown to affect such key dynamical processes as electron transfer and transport, surface dynamics, quantum tunneling, control and nonadiabatic effects. More generally, scientists in many disciplines, from physics through biology to social sciences, have developed increasingly powerful methods of modelling *open systems*, which interact with their environment.

In many nano-scale systems the noise influencing the dynamics arises from quantum fluctuations. Already in 1928, when Nyquist proposed the fluctuation-dissipation theorem [4], the quantum fluctuations were treated differently than the classical ones: the energy $k_B T$ from the classical equipartition law was replaced by the thermally averaged energy of a quantum harmonic oscillator, a distinction becoming negligible at high temperatures. This result has been followed by the development of the new branch of physics, the theory of *open quantum systems* [6–8]. It has found applications in almost all areas of natural sciences [9], from quantum optics [10], through condensed matter physics [11], nanotechnology [12] and spintronics [13], through quantum information [14], through chemistry [15], to biology [16] or even stochastic gravity and inflationary cosmology [17]. Furthermore, it has implications for such fundamental problems as the quantum measurement theory [18] and the emergence of classicality due to decoherence [19].

There exists a rich variety of methods of modelling open quantum systems, applicable to different physical regimes and based on different approximation techniques [20–27]. In this paper we propose a new method, which describes finite-dimensional quantum systems interacting with non-Markovian quantum harmonic oscillator baths. It handles large or infinite baths and a wide range of interaction strengths, while having moderate computational requirements. It uses the Heisenberg picture, which makes it particularly easy to focus the attention on the system degrees of freedom while preserving the decoherence effects due to the coupling to the bath.

In the following section we will remind shortly the theoretical background of our research and the employed formalism (Secs. II A and II B). Next we will present the derivation of the Reduced Matrix Approximation approach (Sec. II C) and propose its two variants: low and high-order in the systems and bath operators. They will be optimised for typical cases of continuous and Lorentzian baths in Sec. II D. In Sec. III we will present the results of our method and compare it to other known techniques of modelling open quantum systems, like the pseudomode method or the quantum state diffusion. Section IV contains a short summary of our work.

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*Electronic address: `a.werpachowska@ucl.ac.uk`

II. THEORETICAL APPROACH

Most generally, an open quantum system is a subsystem of a larger, interacting quantum system, e.g. one of the photons in an EPR pair, an atom in a resonant cavity, a quantum dot interacting with phonons in the crystal or any real object "becoming classical" through scattering of a vast number of air molecules and photons on it. We consider the case of a finite-dimensional quantum system coupled to an infinite-dimensional quantum bath, composed of a possibly infinite number of modes. In such an asymmetrical setup it is natural to ignore the details of the bath dynamics and focus on the reduced density matrix of the system. In this chapter we derive this quantity using the proposed Reduced Operator Approximation approach.

A. Open quantum system

We consider a quantum system represented in an N-dimensional Hilbert space $\mathcal{H}_s$ spanned by basis states $\{|n\rangle\}$. Its internal dynamics is described by the Hamiltonian

$$H_s = \sum_{m,n=1}^{N} V_{mn} t_{mn},$$

where $t_{mn} := |m\rangle\langle n|$ are transition operators between the states $|n\rangle$ and $|m\rangle$ and $\overline{V_{mn}} = V_{nm}$. In a more concise notation, H_s is a trace of an $N \times N$ matrix product:

$$H_s = \operatorname{Tr} \hat{V}^T \hat{t},$$

where $\hat{t}$ is a matrix of system operators, $(\hat{t})_{mn} := t_{mn}$. The Hermitian conjugate of a matrix of operators $\hat{O}$ is defined as $(\hat{O}^\dagger)_{mn} := O_{nm}^\dagger$. In the case of $\hat{t}$, this leads to $\hat{t}^\dagger = \hat{t}$, since $t_{mn}^\dagger = t_{mn}$.

The system is coupled to a quantum bath composed of a collection of K independent harmonic oscillators living in an infinite-dimensional Hilbert space $\mathcal{H}_b$,

$$H_b = \sum_{k=1}^{K} \omega_k a_k^\dagger a_k,$$

where a_k is the annihilation operator of the k-th mode ($\hbar \equiv 1$). The coupling between the system and the bath is described by the operator

$$H_i = \sum_{k=1}^{K} \left(\operatorname{Tr} \hat{g}_k \hat{t} \right) a_k^\dagger + \text{h.c}, \tag{1}$$

where $(\hat{g}_k)_{mn} = \delta_{mn} g_{kn}$ is an $N \times N$ matrix describing the coupling of the k-th bath mode with the system. The fact that each $\hat{g}_k$ is diagonal means that the bath does not induce transitions between system basis states. However, the matrix notation allows for easy generalisation of the model to include such bath-induced transitions. For any type of bath, we can define a spectral density function

$$\hat{J}(\omega) = \sum_k \hat{g}_k^\dagger \hat{g}_k \delta(\omega - \omega_k).$$

The total Hamiltonian, generating the evolution of the system and bath in the Schrödinger picture, is given by

$$H = H_s + H_b + H_i =$$
$$\operatorname{Tr} \hat{V}^T \hat{t} + \sum_{k=1}^{K} \omega_k a_k^\dagger a_k + \operatorname{Tr} \sum_{k=1}^{K} \left(a_k^\dagger \hat{g}_k + a_k \hat{g}_k^\dagger \right) \hat{t}, \tag{2}$$

where we have employed the fact that bath and system operators commute and $\hat{t}^\dagger = \hat{t}$.

The reduced matrix density of the system, $\rho_s(t)$, is defined as

$$\rho_s(t) := \operatorname{Tr}_b \rho(t),$$

where $\rho(t)$ is the density matrix of the system and the bath as a whole, and the trace goes over the bath degrees of freedom only. From the fact that operators t_{mn} correspond to transitions between system basis states, it follows that $\rho_s(t)$ can also be computed from the formula

$$\rho_s(t) = \operatorname{Tr} \rho(t)\hat{t}, \tag{3}$$

where the trace is applied to each operator in the $\rho(t)\hat{t}$ matrix of operators and taken over both system and bath degrees of freedom. The main task of the presented method is obtaining $\rho_s(t)$ without calculating $\rho(t)$.

B. Dynamics in the Heisenberg picture

In the Heisenberg picture the wavefunction is time-independent, $\Psi \equiv \Psi(0)$ (hence, the density matrix of a system in mixed state is time-independent as well), while an observable O (time-independent in the Schrödinger picture) satisfies

$$\frac{d}{dt} O(t) = i[H, O(t)], \tag{4}$$

where $O(t) := e^{iHt} O e^{-iHt}$. From the last definition it follows that $[O_1(t), O_2(t)] = [O_1, O_2](t)$.

We assume that at time $t = 0$ the system and the bath—denoted by their initial reduced density matrices ρ_s and ρ_b, respectively—are uncorrelated. Hence, $\rho = \rho_s \otimes \rho_b$ and Eq. (3) acquires the form

$$\rho_s(t) = \operatorname{Tr}_b \hat{t}(t)\rho = \operatorname{Tr}_s[\rho_s \operatorname{Tr}_b \rho_b \hat{t}(t)]. \tag{5}$$

Let $\hat{t}(t)$ and $a_k(t)$ denote the Heisenberg-picture counterparts of $\hat{t}$ and a_k, respectively, with $\hat{t}(0) := \hat{t}$ and $a_k(0) := a_k$. In order to derive their equations of motions using Eq. (4) we calculate, for any $\hat{A} \in \mathbb{C}^{N \times N}$,

$$[\operatorname{Tr}(\hat{A}\hat{t}(t)), t_{mn}(t)] = \sum_{m',n'=1}^{N} A_{m'n'}[t_{n'm'}(t), t_{mn}(t)]$$
$$= [\hat{A}, \hat{t}(t)]_{mn}, \tag{6}$$

where we have used the identity (valid also in the Schrödinger picture)

$$t_{mn}(t)t_{m'n'}(t) \equiv t_{mn'}(t)\delta_{nm'} \,. \qquad (7)$$

In the matrix-of-operators notation, $[\mathrm{Tr}(\hat{A}\hat{t}(t)), \hat{t}(t)] = [\hat{A}, \hat{t}]$. The above identities can be applied to equation (4) to obtain the evolution of $\hat{t}$ and $\hat{a}$ operators generated by the Hamiltonian (2). For the system we obtain

$$\dot{\hat{t}}(t) = i[\hat{V}^T, \hat{t}(t)] + i\sum_{k=1}^{K}\left([\hat{g}_k, \hat{s}_k^\dagger(t)] + [\hat{g}_k^\dagger, \hat{s}_k]\right), \qquad (8)$$

where $\hat{s}_k(t) := \hat{t}(t)a_k(t)$ are system-bath interaction operators and, since $\hat{t}^\dagger(t) = \hat{t}(t)$ and bath operators commute with system operators, $\hat{s}_k^\dagger(t) = \hat{t}(t)a_k^\dagger(t)$. For the bath, using the canonical commutation relations for bosonic creation/annihilation operators, we obtain

$$\dot{a}_k(t) = -i\omega_k a_k(t) - i\,\mathrm{Tr}\,\hat{g}_k\hat{t}(t)\,. \qquad (9)$$

C. Reduced Operator Approximation

1. General description

The aim of the presented method is to model the evolution of the system, including its decoherence caused by the interaction with the bath. This information is contained in the reduced density matrix of the system $\rho_s(t)$. As demonstrated in previous sections, Eqs (3) and (5), it can be obtained from the mean values of system operators $\hat{t}(t)$. Thus, to calculate $\rho_s(t)$ in the Heisenberg picture, one has to evolve $\hat{t}(t)$ in time. Additionally, since the evolution equation for $\hat{t}(t)$ (8) involves the bath operators $a_k(t)$, due to the system-bath interaction, it is necessary to evolve $a_k(t)$ as well. However, a numerical description of both groups of operators in the total system and bath basis is impossible, as $\mathcal{H}_b$ is infinite-dimensional.

According to Eq. (5), given the initial system state ρ_s we only need to know the partial traces of system operators, $\mathrm{Tr}_b\,\rho_b\hat{t}(t)$, to obtain $\rho_s(t)$. The corresponding partial traces of the bath operators, $\mathrm{Tr}_b\,\rho_b a_k(t)$, contain part of the information on how interaction correlated the bath and the system—if there was no such correlation, $\mathrm{Tr}_b\,\rho_b a_k(t)$ would be proportional to an identity operator in $\mathcal{H}_s$. Thus, even after tracing out the bath degrees of freedom, we can at least approximately capture the system-bath correlations arising from the interaction terms in Eqs. (8) and (9). This observation forms the basis of the proposed Reduced Operator Approximation (ROA).

We represent both system and bath operators by $N \times N$ complex matrices in the system state basis (hence, $\hat{t}$ is represented by a matrix of matrices). Let $M[O(t)]$ denote this *reduced representation* of an operator $O(t)$ with its elements defined as

$$M[O(t)]_{mn} := \mathrm{Tr}_b\,\rho_b\langle m|O(t)|n\rangle\,. \qquad (10)$$

From the definition, $M[O(t)^\dagger] = M[O(t)]^\dagger$.

The evolution equations for the reduced representations of system and bath operators are

$$\frac{d}{dt}M[a_k(t)] = -i\omega_k M[a_k(t)] - i\,\mathrm{Tr}\,\hat{g}_k M[\hat{t}](t) \qquad (11)$$

and

$$\frac{d}{dt}M[\hat{t}(t)] = i[\hat{V}^T, M[\hat{t}(t)]] + \\ i\sum_{k=1}^{K}\left([\hat{g}_k, M[\hat{s}_k^\dagger(t)]] + [\hat{g}_k^\dagger, M[\hat{s}_k(t)]]\right)\,. \qquad (12)$$

Since the system and the bath are correlated, $M[\hat{s}_k(t)] \neq M[\hat{t}(t)]M[a_k(t)]$, which means that the above evolution equations are not complete. The simplest way to complete them is to approximate $M[\hat{s}_k(t)]$ by the product of $M[\hat{t}(t)]$ and $M[a_k(t)]$. However, again due to the system-bath coupling, $M[\hat{t}(t)]M[a_k(t)] \neq M[a_k(t)]M[\hat{t}(t)]$, even though $[\hat{t}(t), a_k(t)] = 0$. Thus, we need to specify a concrete ordering of the multiplied reduced operators. We use the approximations of the form

$$M[\hat{s}_k(t)] \approx \theta M[\hat{t}(t)]M[a_k(t)] + (1-\theta)M[a_k(t)]M[\hat{t}(t)]\,,$$
$$M[\hat{s}_k^\dagger(t)] \approx \theta M[a_k(t)]^\dagger M[\hat{t}(t)] + (1-\theta)M[\hat{t}(t)]M[a_k(t)]^\dagger\,,$$

for $\theta \in [0,1]$. Numerical experiments have shown that simulations diverge for $\theta \neq \frac{1}{2}$. Appendix A contains a simple theoretical explanation of this fact. Choosing $\theta = \frac{1}{2}$, we arrive at the final form of evolution equation of the system operators in the reduced representation,

$$\frac{d}{dt}M[\hat{t}(t)] = i[\hat{V}^T, M[\hat{t}(t)]] \\ + \frac{i}{2}\sum_{k=1}^{K}[\hat{g}_k, \{M[\hat{t}(t)], M[a_k^\dagger(t)]\}] \\ + \frac{i}{2}\sum_{k=1}^{K}[\hat{g}_k^\dagger, \{M[\hat{t}(t)], M[a_k(t)]\}]\,. \qquad (13)$$

Equations (11) and (13) employ reduced representations which are linear in the system or bath operators. Hence, we will refer to them as the *lower-order* ROA.

Additional information about the system-bath correlations is provided by the $M[\hat{s}_k(t)]$ matrix. Hence, it is beneficial to evolve it separately in addition to $M[a_k(t)]$ and $M[\hat{t}(t)]$. For this purpose, we first derive the evolution equation for $\hat{s}_k(t)$, using Eqs. (8) and (9),

$$\frac{d}{dt}\hat{s}_k(t) = \hat{t}(t)\frac{d}{dt}a_k(t) + \left(\frac{d}{dt}\hat{t}(t)\right)a_k(t)$$
$$= i[\hat{V}^T, \hat{s}_k(t)] + i\sum_{k'=1}^{K}[\hat{g}_{k'}^\dagger, \hat{s}_k(t)]a_{k'}(t)$$
$$+ i\sum_{k'=1}^{K}a_{k'}^\dagger(t)[\hat{g}_{k'}, \hat{s}_k(t)] - i\omega_k\hat{s}_k(t) - i\hat{t}(t)\hat{g}_k\,,$$

where we have used the fact that, due to the associativity of the operator product, $\hat{s}_{k'}(t)a_k(t) = \hat{t}(t)a_{k'}(t)a_k(t) = a_{k'}(t)\hat{s}_k(t)$ and $\hat{s}_{k'}^\dagger(t)a_k(t) = a_{k'}^\dagger(t)\hat{s}_k(t)$. To derive the evolution equation for $M[\hat{s}_k(t)]$, we have to solve a similar ordering problem as in the lower-order method. Differently than in the case of Eq. (13), in the evolution equation for $M[\hat{s}_k(t)]$ we do not symmetrise the reduced operator products, and obtain $M[\hat{s}_k(t)a_{k'}(t)] \approx M[\hat{s}_k(t)]M[a_{k'}(t)]$ and $M[a_{k'}^\dagger(t)\hat{s}_k(t)] \approx M[a_{k'}^\dagger(t)]M[\hat{s}_k(t)]$. A simple argument justifying this approach can be found in Appendix A (we have also tested it for numerical stability). Furthermore, due to the aforementioned associativity of the operator product, $M[\hat{s}_k(t)a_{k'}(t)]$ can be approximated by either $M[\hat{s}_k(t)]M[a_{k'}(t)]$, as above, or $M[\hat{s}_{k'}(t)]M[a_k(t)]$. Similarly, we can choose between $M[a_{k'}^\dagger(t)]M[\hat{s}_k(t)]$ and $M[\hat{s}_{k'}^\dagger(t)]M[a_k(t)]$ for $M[a_{k'}^\dagger(t)\hat{s}_k(t)]$. To exploit fully the information about the system-bath correlations contained in $M[\hat{s}_{k'}(t)]$ matrices, we use an equally weighted average of the two approximations. In this way we obtain the evolution equation for the reduced representation of the interaction operator

$$\frac{d}{dt}M[\hat{s}_k(t)] = i[\hat{V}^T, M[\hat{s}_k(t)]] +$$

$$\frac{i}{2}\sum_{k'=1}^{K}\left([\hat{g}_{k'}, M[\hat{s}_{k'}^\dagger(t)]] + [\hat{g}_{k'}^\dagger, M[\hat{s}_{k'}(t)]]\right)M[a_k(t)]$$

$$+ \frac{i}{2}\sum_{k'=1}^{K}M[a_{k'}^\dagger(t)][\hat{g}_{k'}, M[\hat{s}_k(t)]] \qquad (14)$$

$$+ \frac{i}{2}\sum_{k'=1}^{K}[\hat{g}_{k'}^\dagger, M[\hat{s}_k(t)]]M[a_{k'}(t)]$$

$$- i\omega_k\hat{s}_k(t) - i\hat{t}(t)\hat{g}_k.$$

Together with Eqs. (12) and (14) it defines the *higher-order* ROA.

2. Reduced system density matrix

From evolution equations (12) or (13) we instantly see that, since the trace of every commutator is zero,

$$\frac{d}{dt}\left(\operatorname{Tr}M[\hat{t}(t)] \equiv \sum_{m=1}^{N}M[t_{mm}(t)]\right) = 0.$$

Inserting $M[\hat{t}(t)]$ instead of $\hat{t}(t)$ in Eq. (5), we obtain a trace-conserving expression for the reduced density matrix of the system,

$$\rho_s(t) = \operatorname{Tr}\rho_s M[\hat{t}(t)]. \qquad (15)$$

However, if we use it to calculate $\rho_s(t)$, its positivity is not guaranteed. To fix this problem, we make use of the identity (7) to derive

$$\hat{t}(t)\hat{t}(t) \equiv N\hat{t}(t)$$

and replace Eq. (5) with a *different* approximation

$$\rho_s(t) = \frac{1}{N}\operatorname{Tr}\rho_s M[\hat{t}(t)]^2. \qquad (16)$$

Since $t_{mm'}(t)t_{m'n}(t) = t_{mm'}(t)(t_{nm'}(t))^\dagger$ (and the same for the reduced representations), the above formula guarantees that $\rho_s(t)$ is positive-semidefinite. On the other hand, the density matrix (16) does not possess a conserved trace due to the fact that $M[\hat{t}(t)]^2 \neq M[\hat{t}(t)\hat{t}(t)]$. Thus, we normalise the density matrix to obtain

$$\rho_s(t) = \frac{\operatorname{Tr}\rho_s M[\hat{t}(t)]^2}{\operatorname{Tr}[\operatorname{Tr}\rho_s M[\hat{t}(t)]^2]}.$$

D. Baths with continuous spectral densities

In the limit of an infinite number of modes, spectral density $\hat{J}(\omega)$ can be a continuous function. One way to handle this situation is to discretise $\hat{J}(\omega)$ into a finite, but large number of modes. Assuming a constant mode frequency spacing $\Delta\omega$, we define a coupling constant for $\omega = k\Delta\omega$ to be

$$\hat{g}_k = \sqrt{\Delta\omega\hat{J}(k\Delta\omega)}. \qquad (17)$$

Taking the square root ensures proper normalisation as $\Delta\omega \to 0$. For a spectral density being a single Lorentzian peak, the method converges quite well already for $K = 100$ modes per site and $\Delta\omega \approx \gamma/100$, where γ is the half-width at half-maximum of the peak.

1. Independent baths with continuous spectral densities

When each system basis state is coupled to its own independent bath with a continuous spectral density, a more sophisticated method is to describe these baths in terms of collective mode excitations caused by the coupling with the system.

Let us consider bath operators multiplied by their phase factors, $e^{i\omega_k t}a_k(t)$, with dynamics given by $\frac{d}{dt}(e^{i\omega_k t}a_k(t)) = -i\operatorname{Tr}\hat{g}_k\hat{t}(t)e^{i\omega_k t}$. Employing the fact that trace and integration commute, we obtain

$$a_k(t) = e^{-i\omega_k t}a_k(0) - i\int_0^t ds\, e^{-i\omega_k(t-s)}\operatorname{Tr}\hat{g}_k\hat{t}(s),$$

which we insert into the definition of $\hat{s}_k(t)$,

$$\hat{s}_k(t) = e^{-i\omega_k t}\hat{t}(t)a_k(0) - i\hat{t}(t)\int_0^t ds\, e^{-i\omega_k(t-s)}\operatorname{Tr}\hat{g}_k\hat{t}(s)$$

$$= e^{-i\omega_k t}\hat{t}(t)a_k(0) + \hat{u}_k(t),$$

and then the above formula into Eq. (8),

$$\dot{\hat{t}}(t) = i[\hat{V}^T, \hat{t}(t)] + i\sum_{k=1}^{K}\left([\hat{g}_k, \hat{u}_k^\dagger(t)] + [\hat{g}_k^\dagger, \hat{u}_k(t)]\right)$$

$$+ i\sum_{k=1}^{K}\left(e^{i\omega_k t}a_k^\dagger(0)[\hat{g}_k, \hat{t}(t)] + e^{-i\omega_k t}[\hat{g}_k^\dagger, \hat{t}(t)]a_k(0)\right).$$

If each bath has an independent spectral density, each bath mode k is coupled to exactly one basis state n_k, i.e. $(\hat{g}_k)_{mn} = g_{kn_k}\delta_{m,n_k}\delta_{n,n_k}$. Hence,

$$\frac{d}{dt}t_{mn}(t) = i\sum_{m'=1}^{N}(V_{m'm}t_{m'n}(t) - V_{nm'}t_{mm'}(t)) + t_{mn}(t)\times$$

$$\sum_{k=1}^{K}\left[\int_0^t e^{-i\omega_k(t-s)}(|g_{km}|^2 t_{mm}(s) - |g_{kn}|^2 t_{nn}(s))ds - \text{h.c.}\right]$$

$$+ t_{mn}(t)\sum_{k=1}^{K}\left[(\overline{g_{km}} - \overline{g_{kn}})e^{-i\omega_k t}a_k(0) + \text{h.c.}\right],$$

where we have used the fact that for independent densities, $g_{kn}\overline{g_{km}} \neq 0$ only for $n = m$. In the limit of infinite number of modes, using Eq. (17) we obtain

$$\lim_{K\to\infty}\sum_{k=1}^{K}e^{-i\omega_k(t-s)}|g_{km}|^2 = \alpha_m(t-s),$$

where $\alpha_m(\tau) := \int d\omega J_m(\omega)e^{-i\omega\tau}$ is the bath correlation function. In this way we obtain a closed system of differential-integral equations for $t_{mn}(t)$,

$$\frac{d}{dt}t_{mn}(t) = i\sum_{m'=1}^{N}(V_{m'm}t_{m'n}(t) - V_{nm'}t_{mm'}(t)) \qquad (18)$$
$$+ t_{mn}(t)\left[\sqrt{\kappa_m}\tilde{a}_m(t) - \sqrt{\kappa_n}\tilde{a}_n(t) - \text{h.c.}\right]$$

where

$$\tilde{a}_m(t) := \frac{i}{\sqrt{\kappa_m}}\lim_{K\to\infty}\sum_{k=1}^{K}\overline{g_{km}}a_k(t) =$$

$$\frac{i}{\sqrt{\kappa_m}}\lim_{K\to\infty}\sum_{k=1}^{K}\overline{g_{km}}e^{-i\omega_k t}a_k(0) + \int_0^t \frac{\alpha_m(t-s)}{\sqrt{\kappa_m}}t_{mm}(s)ds$$

$$\text{and}\quad \kappa_m := \lim_{K\to\infty}\sum_{k=1}^{K}|g_{km}|^2 = \int_{-\infty}^{\infty}J_m(\omega)d\omega.$$

Operators $\tilde{a}_m^\dagger(t)$ and $\tilde{a}_m(t)$ satisfy canonical commutation relations for bosons,

$$[\tilde{a}_m(t), \tilde{a}_n(t)] = 0,$$

$$[\tilde{a}_m^\dagger(t), \tilde{a}_n(t)] = -\frac{\delta_{mn}}{\sqrt{\kappa_m\kappa_n}}\lim_{K\to\infty}\sum_{k=1}^{K}\overline{g_{kn}}g_{km} = -\delta_{mn}.$$

They are *pseudomode* creation and annihilation operators, creating or destroying collective excitations in a single bath [27]. Their dynamics is given by the equation

$$\frac{d}{dt}\tilde{a}_m(t) = \lim_{K\to\infty}\sum_{k=1}^{K}\overline{g_{km}}\frac{\omega_k e^{-i\omega_k t}a_k(0)}{\sqrt{\kappa_m}} + \frac{\alpha_m(0)}{\sqrt{\kappa_m}}t_{mm}(t)$$

$$+ \kappa_m^{-1/2}\int_0^t t_{mm}(s)\left(\frac{d}{dt}\alpha_m(t-s)\right)ds. \qquad (19)$$

Using the proposed method we have reduced significantly the number of bath operators, from K to N (for independent baths $K \geq N$, while in many cases $K \gg N$). However, numerical simulation of the differential-integral equation for the evolution of the reduced representation of $\tilde{a}_m(t)$ is difficult. In the next section we show that for a particular form of the spectral density function $J_m(\omega)$ one can get rid of the explicit time integration at the cost of a moderate increase of the number of simulated bath operators.

2. Lorentzian spectral densities

Continuous spectral densities composed of Lorentzian peaks,

$$J_n(\omega) = \sum_j \frac{\Gamma_{nj}}{\pi}\frac{\gamma_{nj}}{(\omega - \omega_{nj})^2 + \gamma_{nj}^2}, \qquad (20)$$

are especially popular due to their analytical tractability. In this section, we will optimise our method for this type of the system-bath coupling. The corresponding correlation function is $\alpha_m(\tau) = \sum_j \Gamma_{mj}e^{-i\omega_{mj}\tau - \gamma_{mj}|\tau|}$. Hence, for $t - s > 0$,

$$\frac{d}{dt}\alpha_m(t-s) = -\sum_j \Gamma_{mj}(i\omega_{mj} + \gamma_{mj})e^{-i\omega_{mj}(t-s) - \gamma_{mj}(t-s)}.$$

A continuous spectral density of the form (20) is constructed from an infinite number of independent harmonic oscillator modes, with different modes contributing to each Lorentzian peak. To derive the evolution equation for pseudomode bath operators we express them as sums of $\sum_j \tilde{a}_{mj}(t)$, where $\tilde{a}_{mj}(t)$ is constructed as

$$\tilde{a}_{mj}(t) = \frac{i}{\sqrt{\Gamma_{mj}}}\lim_{K\to\infty}\sum_{k\in P_j^K}\overline{g_{km}}a_k(t),$$

and $P_j^K \subset [1, \ldots, K]$ is the set of indices of modes building the j-th peak, $\cup_j P_j^K = [1, \ldots, K]$ and $P_j^K \cap P_{j'}^K = \delta_{jj'}P_j^K$. This leads directly to $[t_{mn}(t), \tilde{a}_{m'j'}(t)] = 0$, $[\tilde{a}_{mj}(t), \tilde{a}_{nj'}(t)] = 0$ and $[\tilde{a}_{mj}^\dagger(t), \tilde{a}_{nj'}(t)] = -\delta_{mn}\delta_{jj'}$. Thus, $\tilde{a}_{mj}^\dagger(t)$ and $\tilde{a}_{mj}(t)$ are pseudomode creation and annihilation operators corresponding to individual Lorentzian peaks in bath spectral densities.

Comparing $\tilde{a}_{mj}(t)$ with $\tilde{a}_m(t)$ leads to

$$\tilde{a}_{mj}(t) = \frac{i}{\sqrt{\Gamma_{mj}}}\lim_{K\to\infty}\sum_{k\in P_j^K}\overline{g_{km}}e^{-i\omega_k t}a_k(0)$$

$$+ \sqrt{\Gamma_{mj}}e^{(-i\omega_{mj}-\gamma_{mj})t}\int_0^t e^{(i\omega_{mj}+\gamma_{mj})s}t_{mm}(s)ds.$$

Differentiating over t gives

$$\frac{d}{dt}\tilde{a}_{mj}(t) = \lim_{K\to\infty}\sum_{k\in P_j^K}\frac{\overline{g_{km}}\omega_k e^{-i\omega_k t}}{\sqrt{\Gamma_{mj}}}a_k(0) \qquad (21)$$

$$+ (-i\omega_{mj} - \gamma_{mj})\tilde{a}_{mj}(t) + \sqrt{\Gamma_{mj}}t_{mm}(t),$$

with the initial condition

$$\tilde{a}_{mj}(0) = \frac{i}{\sqrt{\Gamma_{mj}}} \lim_{K\to\infty} \sum_{k\in P_j^K} \overline{g_{km}} a_k(0).$$

By splitting $\tilde{a}_m(t)$ into a sum of $\tilde{a}_{mj}(t)$, we have simplified the differential-integral evolution equation (19). In the reduced representation,

$$\frac{d}{dt}M[\tilde{a}_{mj}(t)] = (-i\omega_{mj}-\gamma_{mj})M[\tilde{a}_{mj}(t)]+\sqrt{\Gamma_{mj}}M[t_{mm}(t)]$$

$$(22)$$

with the initial condition $M[\tilde{a}_{mj}(0)] = 0$.

Since $M[t_{mn}(t)\tilde{a}_{m'j}(t)] \neq M[t_{mn}(t)]M[\tilde{a}_{m'j}(t)]$, we evolve separately the reduced representation of operator products $s_{mnm'j}(t) := t_{mn}(t)\tilde{a}_{m'j}(t) = i\Gamma_{m'j}^{1/2}\lim_{K\to\infty}\sum_k{}'\overline{g_{km'}}s_{mnk}(t)$. Its adjoint equals $s_{mnm'j}^{\dagger}(t) = t_{nm}(t)\tilde{a}_{m'j}^{\dagger}(t)$. The relevant commutators are $[s_{mnm'j}(t),\tilde{a}_{m''j'}(t)] = 0$ and $[s_{mnm'j}^{\dagger}(t),\tilde{a}_{m''j'}(t)] = -t_{nm}(t)\delta_{m'm''}\delta_{jj'}$.

Evolution equation of the system (18) in the Lorentzian bath acquires the form

$$\frac{d}{dt}t_{mn}(t) = i\sum_{m'=1}^{N}(V_{m'm}t_{m'n}(t) - V_{nm'}t_{mm'}(t))$$
$$+ \sum_j \sqrt{\Gamma_{mj}}\left[s_{mnmj}(t) - s_{nmmj}^{\dagger}(t)\right] \qquad (23)$$
$$+ \sum_j \sqrt{\Gamma_{nj}}\left[s_{nmnj}^{\dagger}(t) - s_{mnnj}(t)\right].$$

Hence, the operators $s_{mnm'j}(t)$ themselves follow the evolution equation

$$\frac{d}{dt}s_{mnm'j}(t) = i\sum_{m''=1}^{N}(V_{m''m}s_{m''nm'j}(t) - V_{nm''}s_{mm''m'j}(t))$$
$$+ \sum_{j'}\sqrt{\Gamma_{mj}}\left[s_{mnmj'}(t) - s_{nmmj'}^{\dagger}(t)\right]\tilde{a}_{m'j}(t)$$
$$+ \sum_{j'}\sqrt{\Gamma_{nj}}\left[s_{nmnj'}^{\dagger}(t) - s_{mnnj'}(t)\right]\tilde{a}_{m'j}(t)$$
$$+ t_{mn}(t)\lim_{K\to\infty}\sum_{k\in P_j^K}\frac{\overline{g_{km'}}\omega_k e^{-i\omega_k t}}{\sqrt{\Gamma_{m'j}}}a_k(0)$$
$$+ (-i\omega_{m'j} - \gamma_{m'j})s_{mnm'j}(t) + \sqrt{\Gamma_{m'j}}\delta_{nm'}t_{mn}(t)$$

$$(24)$$

with the initial condition

$$s_{mnm'j}(0) = \frac{i}{\sqrt{\Gamma_{m'j}}}t_{mn}(0)\lim_{K\to\infty}\sum_k{}'\overline{g_{km'}}a_k(0).$$

Evolution equations for the reduced repretentations of the above system and interaction operators, respectively, are

$$\frac{d}{dt}M[t_{mn}(t)] = i\sum_{m'=1}^{N}(V_{m'm}M[t_{m'n}(t)] - V_{nm'}M[t_{mm'}(t)])$$
$$+ \sum_j \sqrt{\Gamma_{mj}}\left[M[s_{mnmj}(t)] - M[s_{nmmj}^{\dagger}(t)]\right]$$
$$+ \sum_j \sqrt{\Gamma_{nj}}\left[M[s_{nmnj}^{\dagger}(t)] - M[s_{mnnj}(t)]\right]$$

$$(25)$$

and

$$\frac{d}{dt}M[s_{mnm'j}(t)] = i\sum_{m''=1}^{N}(V_{m''m}M[s_{m''nm'j}(t)] -$$
$$V_{nm''}M[s_{mm''m'j}(t)])+$$
$$\frac{1}{2}\sum_{j'}\sqrt{\Gamma_{mj'}}(M[s_{mnmj'}(t)] - M[s_{nmmj'}^{\dagger}(t)])M[\tilde{a}_{m'j}(t)]+$$
$$\frac{1}{2}M[s_{mnm'j}(t)]\sum_{j'}(\sqrt{\Gamma_{mj'}}M[\tilde{a}_{mj'}(t)] - \sqrt{\Gamma_{nj'}}M[\tilde{a}_{nj'}(t)])$$
$$+ \frac{1}{2}\sum_{j'}\sqrt{\Gamma_{nj'}}(M[s_{nmnj'}^{\dagger}(t)] - M[s_{mnnj'}(t)])M[\tilde{a}_{m'j}(t)]-$$
$$\frac{1}{2}\sum_{j'}(\sqrt{\Gamma_{mj'}}M[\tilde{a}_{mj'}^{\dagger}(t)] - \sqrt{\Gamma_{nj'}}M[\tilde{a}_{nj'}^{\dagger}(t)])M[s_{mnm'j}(t)]$$
$$+ (-i\omega_{m'j} - \gamma_{m'j})M[s_{mnm'j}(t)] + \sqrt{\Gamma_{m'j}}\delta_{nm'}M[t_{mn}(t)]$$

$$(26)$$

with initial condition $M[s_{mnm'j}(0)] = 0$. We use the same operator order as in Subsec. II D 1.

Higher-order Lorentzian ROA employs Eqs. (22), (25) and (26). Lower-order Lorentzian ROA describes the bath evolution with Eq. (22). To describe the system evolution, we represent $M[s_{mnm'j}(t)]$ as $\frac{1}{2}\{M[t_{mn}(t)], M[\tilde{a}_{m'j}(t)]\}$, obtaining

$$\frac{d}{dt}M[t_{mn}(t)] = i\sum_{m'=1}^{N}(V_{m'm}M[t_{m'n}(t)] - V_{nm'}M[t_{mm'}(t)])$$
$$+ \frac{1}{2}\Big\{M[t_{mn}(t)], \sum_j\big[\sqrt{\Gamma_{mj}}M[\tilde{a}_{mj}(t)]$$
$$- \sqrt{\Gamma_{nj}}M[\tilde{a}_{nj}(t)] - \text{h.c.}\big]\Big\},$$

$$(27)$$

where the symmetrisation of the matrix product is justified by the same arguments as in Sec. II C 1.

The Lorentzian methods use much lower number of bath and interaction operators than the general ones, because they model the bath excitations as collective pseudomodes. Furthermore, thanks to the analytical integration of the spectral density, they automatically include the tails of the spectral density, which are cut off by the discrete method.

III. NUMERICAL EXAMPLES AND COMPARISON WITH OTHER METHODS

In this section we present an example application of our method to the description of a molecular aggregate interacting with a non-Markovian quantum bath, and compare it with two other techniques: the pseudomode method [27] (PM) and non-Markovian quantum state diffusion [26] (QSD).

The PM method replaces each Lorentzian peak in the spectral density by a pseudomode with a complex frequency, and models the dynamics of the original system and bath by simulating exactly, in the Schrödinger picture, the system interacting with this pseudomode bath. As the reduced density matrix of the system $\rho_s(t)$ obtained in this way is exact, we use the PM method as our reference. The downside of the PM method is that, since it requires an exact simulation of a quantum many-body system, its computational requirements increase exponentially with the number of system basis states and the number of bath spectral density peaks. The other method used for comparison, QSD, is an approximate one, which uses a Monte-Carlo simulation to calculate $\rho_t(s)$. Its main advantage is the slow growth of the computational requirements with the system size.

We model an exciton delocalised on a linear chain composed of $N = 3$ sites coupled by the nearest-neighbour potential, $V_{mn} = -(\delta_{m,n+1} + \delta_{m,n-1})$. Each site interacts with a simple zero-temperature quantum bath with a unimodal Lorentzian spectral density $J(\omega) = \Gamma\gamma\pi^{-1}/((\omega - \omega_0)^2 + \gamma^2)$, where we set $\omega_0 = 1$. We consider four cases:

bath (Fig. 1)	γ	Γ
A) weak narrow	0.1	0.3
B) strong narrow	0.1	1
C) weak wide	0.5	0.3
D) strong wide	0.5	1

The "wide" Lorentzian peaks correspond to fast decreasing bath correlation function, while the "narrow" ones indicate long correlation times. The coupling strength, "strong" or "weak", determines the decoherence rate.

We simulate the reduced density matrix of the system initially in the state $\Psi_s = [1, 0, 0]^T$, and compare the probabilities of finding the system in this state at later times, i.e. $(\rho_s(t))_{11}$. We use three variants of the ROA method: low-order ROA (Sec. II C 1), as well as low and high-order Lorentzian ROA (Sec. II D 2); the high-order ROA has been skiped as the least efficient. The results are plotted in Figs. 2–5. Comparison with the exact PM method shows that the best results are obtained for the Lorentzian variants of the method, which take into account the whole range of the Lorentzian spectral density by analytical integration. At the same time QSD has the tendency to converge too rapidly to a steady state solution, as compared to the exact PM method. The figure captions contain a detailed analysis of the results.
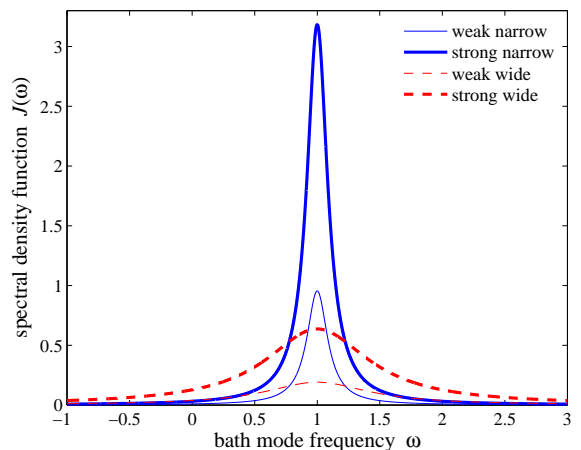

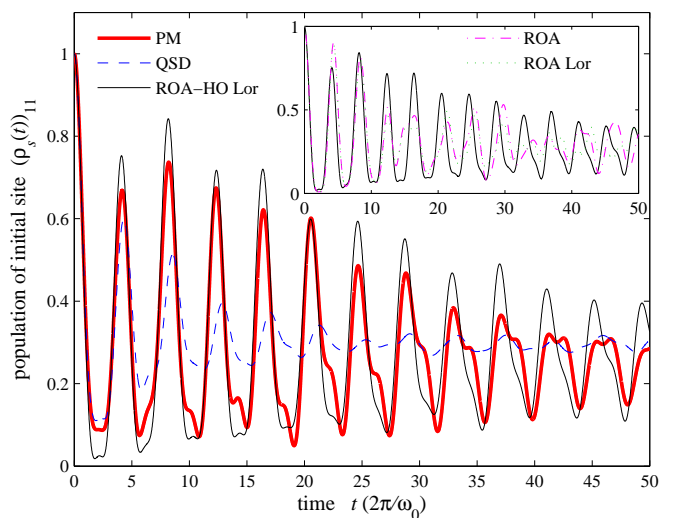FIG. 1: Unimodal Lorentzian spectral densities used in simulations.

FIG. 2: Comparison of the results of the ROA approach with the PM and QSD methods for bath A. The high-order Lorentzian ROA properly reproduced the amplitude and the phase of the probability density oscillations (the inset shows that it is superior to its low order variants). The QSD method dampens the oscillations and does not reconstruct their phase.

For further comparison with the QSD method we calculate the transfer of the excitation on a ring aggregate in multimode Lorentzian bath (see Ref. [28]) in Fig. 6. The results obtained using the low-order Lorentzian ROA method are characterised by a much slower decoherence rate, as shown in the inset. We attribute the faster decoherence observed in the QSD method to the zeroth order functional expansion (ZOFE) [29] required to make the method numerically feasible. It treats each path of the Monte Carlo simulation independently and thus increases artificially the amount of decoherence in the simulation causing the system to converge too rapidly to a steady state solution.
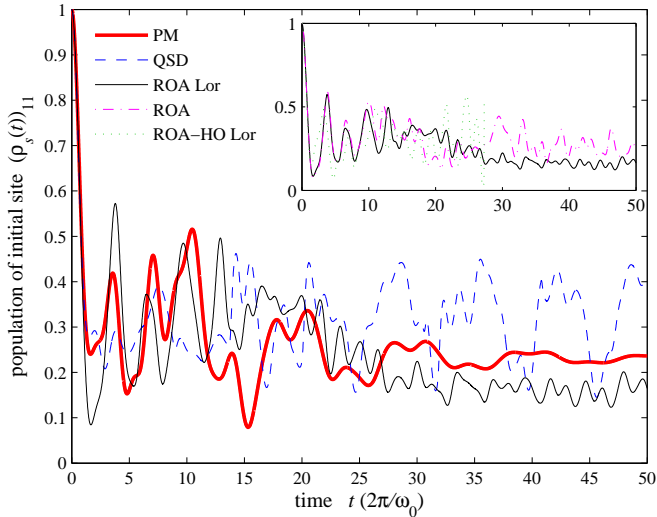
FIG. 3: Comparison of the results of the ROA approach with the PM and QSD methods for bath B. Although none of the methods satisfactorily reconstructs the PM results, the low-order Lorentzian ROA properly describes how the amplitude of fluctuations of the probability density changes in time. The inset presents a comparison of the three variants of ROA method; the high-order Lorentzian ROA diverges.
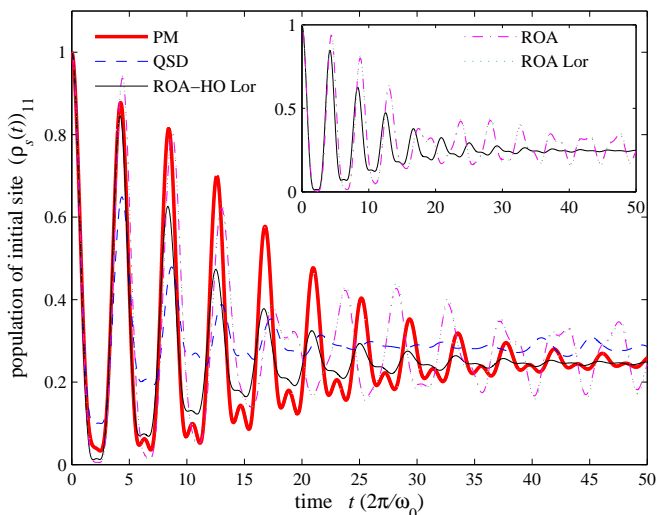

FIG. 4: Comparison of the results of the ROA approach with the PM and QSD methods for bath C. The high-order Lorentzian ROA precisely reconstructs the phase of the probability density oscillations, while its low-order variants reconstruct the amplitude. The QSD method does not describe correctly the amplitude of the oscillations and loses the phase. The inset presents the comparison of the three ROA methods.

IV. SUMMARY

The presented Reduced Operator Approximation is a simple, physically transparent and computationally efficient method of modelling open quantum systems. It employs the Heisenberg picture of the quantum dynam-
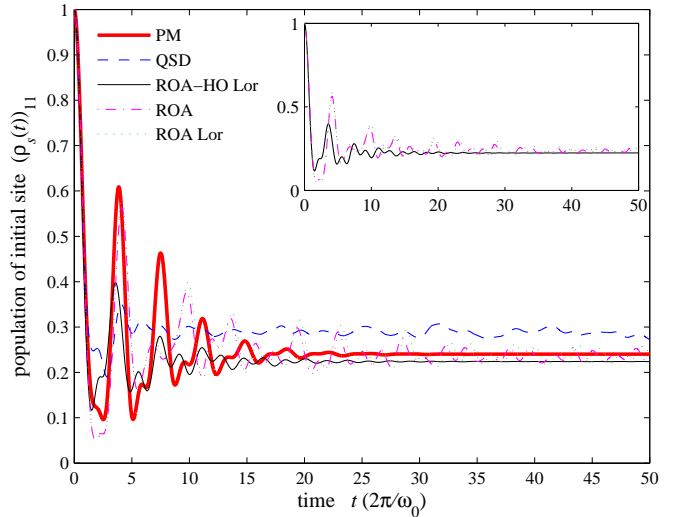

FIG. 5: Comparison of the results of the ROA approach with the PM and QSD methods for bath D. The low-order ROA methods correctly describe the amplitude and phase of the probability density oscillations at shorter times and, together with the high-order Lorentzian ROA (which diminishes the oscillation amplitudes), stabilise at the correct level. The QSD strongly diminishes the oscillations and fails to recover the correct steady state.

ics, which allows us to focus on the system degrees of freedom in a natural and easy way. We have described different variants of the method: the low-order ROA, the high-order ROA (including the interaction operators) and their versions for Lorentzian baths. They have been applied to different systems (coupled to different baths with different strengths). Comparison of our results with the exact pseudomode and the popular quantum state diffusion method favours the ROA approach. Furthermore, the efficiency of ROA (especially the low-order case) is much higher than in the case of PM and QSD approach.

The method has been derived for the simplest case of linear coupling between the system and the bath. However, its general version can be easily extended to higher-order couplings. Its another advantage is that a single simulation of the reduced system operators can be used to generate reduced density matrices for an arbitrary choice of initial system state.
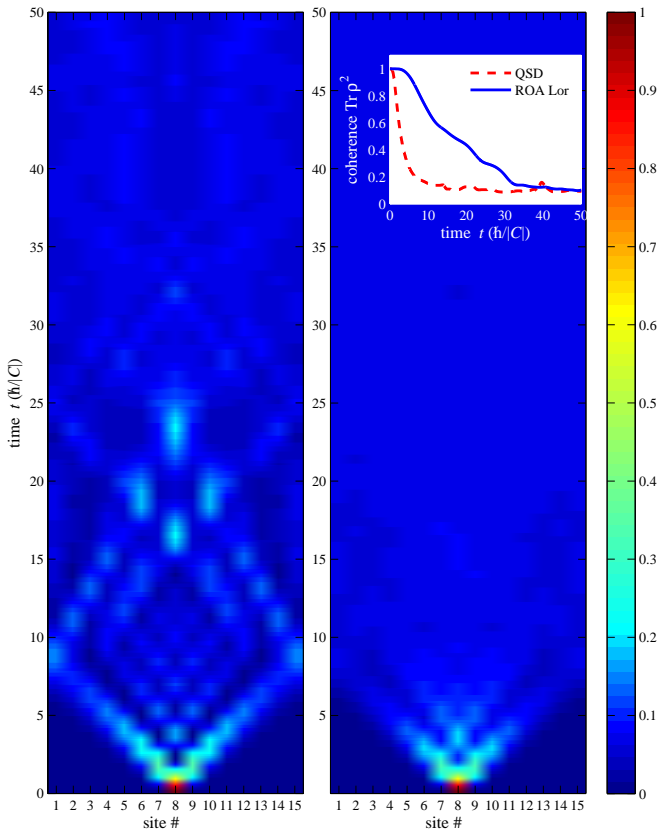
FIG. 6: Comparison of the results of the ROA Lorentzian method with the QSD method for a ring aggregate of 15 sites (initially only the site 8 is excited) in multimode Lorentzian bath (see Ref. [28] for the description of the spectral density and definition of the units used in the plot). Inset: coherence defined as $\mathrm{Tr}\,\rho^2$ calculated using both methods.

APPENDIX A: OPERATOR REPRESENTATION PRODUCTS

Let us consider a Hamiltonian with N sites and N bath modes, $\hat{V} = 0$ and $(\hat{g}_k)_{mn} = g_k \delta_{m,k} \delta_{n,k}$. It is easy to see that in this case the system operators are diagonal and $t_{mm}(t) = t_{mm}(0)$. Hence, we can solve Eq. (9) explicitly, obtaining

$$a_m(t) = e^{-i\omega_m t}\left(a_m(0) - \frac{g_m}{\omega_m}(e^{i\omega_m t} - 1)t_{mm}(t)\right),$$
$$\text{(A1)}$$

and, in the reduced representation,

$$M[a_m(t)] = -\frac{g_m}{\omega_m}(1 - e^{-i\omega_m t})M[t_{mm}(t)]. \quad \text{(A2)}$$

This shows that even in this simple case, the $M[t_{mn}(t)]$ cannot in general commute with $M[a_k(t)]$.

Let us assume that at time t, the relation

$$M[t_{mn}(t)]M[t_{m'n'}(t)] = \delta_{nm'}M[t_{mn'}(t)] \quad \text{(A3)}$$

is preserved. Hence,

$$M[t_{mn}(t)]M[a_k(t)] = -\delta_{nk}\frac{g_n}{\omega_n}(1 - e^{-i\omega_n t})M[t_{mn}(t)],$$
$$M[a_k(t)]M[t_{mn}(t)] = -\delta_{mk}\frac{g_m}{\omega_m}(1 - e^{-i\omega_m t})M[t_{mn}(t)].$$

Applying the above results to Eq. (13), we obtain

$$\frac{d}{dt}M[t_{mn}(t)] = i(1 - \delta_{mn})[\theta(\overline{\alpha_m(t)} - \alpha_n(t)) + (1 - \theta)(\alpha_m(t) - \overline{\alpha_n(t)})]M[t_{mn}(t)] \quad \text{(A4)}$$

where $\alpha_m(t) := -\frac{|g_m|^2}{\omega_m}(1 - e^{-i\omega_m t})$. It easy to see that for $n \neq m'$, $\frac{d}{dt}M[t_{mn}(t)]M[t_{m'n'}(t)] = 0$, consistently with Eq. (A3). For $n = m'$, we have

$$\frac{d}{dt}M[t_{mn}(t)]M[t_{nn'}(t)] = i(1 - \delta_{mn})[\theta(\overline{\alpha_m(t)} - \alpha_n(t))$$
$$+ (1 - \theta)(\alpha_m(t) - \overline{\alpha_n(t)})]M[t_{mn'}(t)]$$
$$+ i(1 - \delta_{nn'})[\theta(\overline{\alpha_n(t)} - \alpha_{n'}(t))$$
$$+ (1 - \theta)(\alpha_n(t) - \overline{\alpha_{n'}(t)})]M[t_{mn'}(t)],$$

while in the case of $m = n$,

$$\frac{d}{dt}M[t_{mn}(t)]M[t_{nn'}(t)] = i(1 - \delta_{mn'})[\theta(\overline{\alpha_m(t)} - \alpha_{n'}(t))$$
$$+ (1 - \theta)(\alpha_m(t) - \overline{\alpha_{n'}(t)})]M[t_{mn'}(t)] = \frac{d}{dt}M[t_{mn'}(t)],$$

again consistently with Eq. (A3). Analogous result is obtained for $n = n'$. However, in the case of $m \neq n$ and $n \neq n'$, we have

$$\frac{d}{dt}M[t_{mn}(t)]M[t_{nn'}(t)] = i[\theta(\overline{\alpha_m(t)} - \alpha_n(t)) +$$
$$(1 - \theta)(\alpha_m(t) - \overline{\alpha_n(t)})]M[t_{mn'}(t)] + i[\theta(\overline{\alpha_n(t)} - \alpha_{n'}(t))$$
$$+ (1 - \theta)(\alpha_n(t) - \overline{\alpha_{n'}(t)})]M[t_{mn'}(t)].$$

It is only for $\theta = 1/2$ that the terms with $\alpha_n(t)$ cancel out and the right side is equal to $\frac{d}{dt}M[t_{mn'}(t)]$. Therefore, for $\theta = 1/2$ evolution equations for $M[t_{mn}(t)]$ preserve product identities for $t_{mn}(t)$. Consequently, we obtain

$$\frac{d}{dt}M[t_{mn}(t)] = i\left[\mathrm{Re}\left(\alpha_m(t) - \alpha_n(t)\right)\right]M[t_{mn}(t)],$$

leading to the solution

$$M[t_{mn}(t)] = M[t_{mn}(0)]\exp(i\int_0^t \mathrm{Re}\left(\alpha_m(s) - \alpha_n(s)\right))ds.$$

For operators $s_{mnk}(t)$, we obtain from Eq. (A1) that

$$M[s_{mnk}(t)] = -\frac{g_n}{\omega_n}\delta_{nk}(1 - e^{-i\omega_n t})M[t_{mn}(t)], \quad \text{(A5)}$$

assuming the bath was in the ground state at $t = 0$. For the simple model considered in this Appendix, their Heisenberg equations are

$$\frac{d}{dt}s_{mnk}(t) = is_{mnk}(t)(\overline{g_m}a_m(t) - \overline{g_n}a_n(t))$$
$$+ i(g_m a_m^\dagger(t) - g_n a_n^\dagger(t))s_{mnk}(t) \quad \text{(A6)}$$
$$- i\omega_k s_{mnk}(t) - i\delta_{nk}g_n t_{mn}(t).$$

It is easy to notice that $s_{mnk}(t)a_{k'}(t) = s_{mnk'}(t)a_k(t)$ and $a_{k'}^\dagger(t)s_{mnk}(t) = s_{nmk'}^\dagger(t)a_k(t)$. From Eqs. (A2) and (A5) we see that this property is preserved in the reduced representation and $M[s_{mnk}(t)]M[a_{k'}(t)] \sim \delta_{nk}\delta_{nk'}M[t_{mn}(t)]$ while $M[a_{k'}^\dagger(t)]M[s_{mnk}(t)] \sim \delta_{nk}\delta_{mk'}M[t_{mn}(t)]$. Thus, when choosing the reduced representation of Eq. (A6) it is irrelevant whether the index k or k' is attached to the s operator on the right side. For simplicity, we keep the k index with the s operators, and use the representations

$$M[s_{mnk}(t)a_{k'}(t)] = \theta M[s_{mnk}(t)]M[a_{k'}(t)] \\ + (1-\theta)M[a_{k'}]M[s_{mnk}(t)],$$

$$M[a_{k'}^\dagger(t)s_{mnk}(t)] = \theta M[a_{k'}(t)]^\dagger M[s_{mnk}(t)] \\ + (1-\theta)\left(M[s_{mnk}(t)]M[a_{k'}]^\dagger - M[t_{mn}(t)]\delta_{k,k'}\right),$$

where $\theta \in [0,1]$. Applying this to Eq. (A6), we obtain

$$\frac{d}{dt}M[s_{mnk}(t)] = i\theta M[s_{mnk}(t)](\overline{g_m}M[a_m(t)] - \overline{g_n}M[a_n(t)]) \\ + i\theta(g_m M[a_m^\dagger(t)] - g_n M[a_n^\dagger(t)])M[s_{mnk}(t)] \\ + i(1-\theta)(\overline{g_m}M[a_m(t)] - \overline{g_n}M[a_n(t)])M[s_{mnk}(t)] \\ + i(1-\theta)M[s_{mnk}(t)](g_m M[a_m^\dagger(t)] - g_n M[a_n^\dagger(t)]) \\ - i(1-\theta)(g_m\delta_{m,k} - g_n\delta_{n,k})M[t_{mn}(t)] \\ - i\omega_k M[s_{mnk}(t)] - i\delta_{nk}g_n M[t_{mn}(t)].$$

Since for $m = n$ the θ-dependent parts are zero, we have to consider the case $m \neq n$ to determine the best choice of θ. Additionally, we assume that $k = m$. From Eq. (A5) we know that $M[s_{mnm}(t)] = 0$. Thus, consistency requires that $\frac{d}{dt}M[s_{mnm}(t)]$ calculated using the above expression should evaluate to zero. Using Eq. (A2) and the above assumptions, we transform it to $\frac{d}{dt}M[s_{mnm}(t)] = -i(1-\theta)g_m M[t_{mn}(t)]$. Thus, consistency requires that we choose $\theta = 1$ to calculate the derivatives of $M[s_{mnk}(t)]$.

[1] Pawel F. Góra. The theory of Brownian motion: A hundred years' anniversary. 52 Special Issue: The 19-th Marian Smoluchowski Symposium on Statistical Physics, Kraków, Poland, pages 52–57, 2006.

[2] Albert Einstein. Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen. *Ann. Phys.*, 17:549–560, 1905.

[3] M. Smoluchowski. Zur kinetischen Theorie der Brownschen Molekularbewegung und der Suspensionen. *Ann. Phys.*, 21:756–780, 1906.

[4] H. Nyquist. Thermal agitation of electric charge in conductors. *Phys. Rev.*, 32:110–113, Jul 1928.

[5] Herbert B. Callen and Theodore A. Welton. Irreversibility and generalized noise. *Phys. Rev.*, 83:34–40, Jul 1951.

[6] A. Isar, A. Sandulescu, H. Scutaru, E. Stefanescu, and W. Scheid. Open quantum systems. *International Journal of Modern Physics E*, 03(02):635–714, 1994.

[7] Hans-Peter Breuer and Francesco Petruccione. *The theory of open quantum systems*. Oxford University Press, 2007.

[8] Á. Rivas and S.F. Huelga. *Open Quantum Systems: An Introduction*. SpringerBriefs in Physics. Springer, 2011.

[9] Heinz-Peter Breuer and Francesco Petruccione. Concepts and methods in the theory of open quantum systems. In Fabio Benatti and Roberto Floreanini, editors, *Irreversible Quantum Dynamics*, volume 622 of *Lecture Notes in Physics*, pages 65–79. Springer Berlin Heidelberg, 2003.

[10] D. F. Walls and G. J. Milburn. *Quantum Optics*. Springer-Verlag, Berlin, 1994.

[11] U. Weiss. *Quantum Dissipative Systems, Volume 2 of Series in Modern Condensed Matter Physics*. World Scientific, Singapore, 1999.

[12] I. O. Kulik and R. Ellialtioglu (Eds.). *Quantum Mesoscopic Phenomena and Mesoscopic, Devices in Microelectronics, NATO Series, Series C: Mathematical and Physical Sciences, Vol. 559*. Kluwer Academic Publishers, Dordrecht, 2000.

[13] D. Loss D.D. Awschalom and N. Samarth (eds.). *Semiconductor Spintronics and Quantum Computation, Series on Nanoscience and Technology*. Springer-Verlag, Berlin, 1992.

[14] M. A. Nielsen and I. L. Chuang. *Quantum Computation and Quantum Information*. Cambridge University Press, Cambridge, 1997.

[15] P. Pechukas and U. Weiss (guest editors). *Quantum Dynamics of Open Systems, Chemical Physics, Special Issue, Vol. 268, Nos. 1-3*. 2001.

[16] Gregory D. Scholes, Graham R. Fleming, Alexandra Olaya-Castro, , and Rienk van Grondelle. Lessons from nature about solar light harvesting. *Nature Chemistry*, pages 763–774, 2011.

[17] Daniel Arteaga. Quantum Brownian representation for the quantum field modes, Advances in High Energy Physics, vol. 2008. *Advances in High Energy Physics*, page 034902, 2009.

[18] V. B. Braginsky and F. Ya. Khalili. *Quantum Measurement*. Cambridge University Press, Cambridge, 1992.

[19] D. Giulini, E. Joos, C. Kiefer, J. Kupsch, I.-

O.Stamatescu, and H. D. Zeh. *Decoherence and the Appearance of a Classical World in Quantum Theory.* Springer-Verlag, Berlin, 1996.

[20] A. Stradomska and P. Petelenz. Intermediate vibronic coupling in sexithiophene single crystals. *Journal of Chemical Physics*, 130(9), 2009.

[21] Ernesto Cota, Ramón Aguado, and Gloria Platero. Erratum: ac-driven double quantum dots as spin pumps and spin filters. *Phys. Rev. Lett.*, 94:229901, 2005.

[22] C.H. Fleming and B.L. Hu. Non-Markovian dynamics of open quantum systems: Stochastic equations and their perturbative solutions. *Annals of Physics*, 327(4):1238 – 1276, 2012.

[23] Jrgen T. Stockburger and Hermann Grabert. Non-Markovian quantum state diffusion. *Chemical Physics*, 268(13):249 – 256, 2001.

[24] Jan Roden, Alexander Eisfeld, Wolfgang Wolff, and Walter T. Strunz. Influence of complex exciton-phonon coupling on optical absorption and energy transfer of quantum aggregates. *Phys. Rev. Lett.*, 103:058301, 2009.

[25] A. Kolli, A. Nazir, and A. Olaya-Castro. Electronic excitation dynamics in multichromophoric systems described via a polaron-representation master equation. *Journal of Chemical Physics*, 135(15), 2011.

[26] L. Diósi, N. Gisin, and W. T. Strunz. Non-Markovian quantum state diffusion. *Phys. Rev. A*, 58:1699–1712, Sep 1998.

[27] Ataç İmamoğlu. Stochastic wave-function approach to non-Markovian systems. *Phys. Rev. A*, 50:3650–3653, Nov 1994.

[28] Jan Roden, Alexander Eisfeld, Wolfgang Wolff, and Walter T. Strunz. Influence of complex exciton-phonon coupling on optical absorption and energy transfer of quantum aggregates. *Phys. Rev. Lett.*, 103:058301, Jul 2009.

[29] Jan Roden, Walter T. Strunz, and Alexander Eisfeld. Non-Markovian quantum state diffusion for absorption spectra of molecular aggregates. *J. Chem. Phys.*, page 034902, 2011.