Reduced density matrix for nonequilibrium steady states: A modified Redfield solution approach

Juzar Thingna,[1,2,*] Jian-Sheng Wang,[1] and Peter Hänggi[1,2]

[1]*Department of Physics and Center for Computational Science and Engineering, National University of Singapore,
Singapore 117551, Republic of Singapore*
[2]*Institut für Physik Universität Augsburg, Universitätsstrasse 1, D-86135 Augsburg, Germany*
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We describe a method to obtain the reduced density matrix (RDM) correct up to second order in system-bath coupling in *nonequilibrium* steady-state situations. The RDM is obtained via a scheme based on analytic continuation, using the time-local Redfield-like quantum master equation, which was earlier used by the same authors [J. Chem. Phys. **136**, 194110 (2012)] to obtain the correct thermal equilibrium description. This nonequilibrium modified Redfield solution is then corroborated with the exact RDM obtained via the nonequilibrium Green's function technique for the quantum harmonic oscillator. Lastly, the scheme is compared to different quantum master equations (QMEs), namely the time-local Redfield-like and the Lindblad-like QMEs, in order to illustrate the differences between each of these approaches.

I. INTRODUCTION

Statistical mechanics [1–4] has been one of the cornerstones of equilibrium physics, which has enabled us to calculate any arbitrary macroscopic property of a system in contact (implicitly assumed to be *weak*) with a giant environment (typically referred to as bath). Even though the framework of statistical mechanics has been highly successful, its nonequilibrium counterpart still eludes the scientific community. Even in the particular case of steady states, the nonequilibrium formulation is predominantly mathematical and formal [5–7] without a *general* prescription to obtain the exact reduced density matrix.

Unlike Gibbs, who searched for a statistical ensemble compatible with equilibrium thermodynamics, we focus on obtaining a nonequilibrium steady-state reduced density matrix compatible with the laws of quantum dynamics. This objective is known under a wider label of open quantum systems [8–11]. The goal is typically addressed by use of a wide variety of formally exact [12–17] or perturbative master equations [18–21]. For the steady-state nonequilibrium scenario all of the perturbative approaches are appropriate only in the regime of vanishing system-bath coupling or in the van Hove limit [22–24]; see Ref. [25] for an elucidate exposition on this limit. Hence, it is crucial to obtain the reduced density matrix (RDM) containing higher orders of the system-bath coupling in order to extract essential information about the physical quantities related to transport.

Our main goal in this paper is to obtain the nonequilibrium *steady-state reduced density matrix* for a general system connected to multiple heat baths up to second order in the system-bath coupling. We achieve this using an analytic continuity technique, which we have introduced previously [24] for the case of thermal equilibrium. For this nontrivial steady-state nonequilibrium case exact results presently exist mainly for transporting currents across classical [26] and quantum harmonic chains [27–30]. It is only recently that Dhar, Saito, and Hänggi [31] have analytically obtained the exact

steady-state RDM of an open system composed of harmonic oscillators. Due to the lack of exact general solutions for anharmonic systems in nonequilibrium steady state, in this work we corroborate our result with the analytic solution of Dhar *et al*. and additionally compare it to other commonly used quantum master equations (QMEs). The deficiencies in those other commonly used QMEs definitely call for an accurate approach such as ours in order to investigate nonequilibrium phenomena for general anharmonic systems.

The paper is organized as follows: In Sec. II we describe our model and the time-local Redfield-like quantum master equation in the presence of multiple baths obtained under the weak system-bath coupling approximation. The central scheme of this paper is briefly described in Sec. III, where we obtain the nonequilibrium modified Redfield solution. Section IV illustrates the numerical implementation of our scheme for the steady-state density matrix of a quantum harmonic oscillator and provides comparison with the exact nonequilibrium Green's function method and the Redfield- and the Lindblad-like QMEs, illustrating some of the pitfalls in these commonly used techniques. In Sec. V we summarize and propose promising further extensions.

II. TIME-LOCAL QUANTUM MASTER EQUATION IN THE PRESENCE OF MULTIPLE BATHS

Our basic model is similar to that used by many researchers in the field of transport and goes under a wider label of the Magalinskiĭ-Zwanzig-Caldeira-Leggett model [32–35] in the field of quantum dissipation. The total Hamiltonian comprises of multiple baths and a system and is written as follows:

$$H_{\text{tot}} = H_{\text{S}} + \sum_{\alpha} (H_{\alpha} + H_{\text{R}\alpha} + H_{\text{S}\alpha}), \tag{1}$$

where H_{S} denotes the generally anharmonic system Hamiltonian. Here

$$H_{\alpha} = \sum_{k=1}^{\infty} \left(\frac{p_{k,\alpha}^2}{2m_{k,\alpha}} + \frac{m_{k,\alpha}\,\omega_{k,\alpha}^2}{2} x_{k,\alpha}^2 \right), \tag{2}$$

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*juzar.thingna@physik.uni-augsburg.de

describes the α-th bath as an infinite collection of harmonic oscillators, each having a mass $m_{k,\alpha}$ and a frequency $\omega_{k,\alpha}$. The above description of the baths being of the harmonic form is one particular choice which helps us concretize the description below, but by no means is it a restriction to our approach and one could, in general, choose fermionic or spin baths [36–39]. The potential renormalization term is given by

$$H_{\mathrm{R}\alpha} = (Y^\alpha)^2 \left(\frac{1}{2} \sum_{k=1}^\infty \frac{c_{k,\alpha}^2}{m_{k,\alpha}\,\omega_{k,\alpha}^2} \right), \qquad (3)$$

where Y^α denotes any function of the system variables connected to the α-th bath and $c_{k,\alpha}$ denotes the coupling constant of the k-th oscillator with the system operator Y^α. The renormalization term above occurs naturally when one needs to ensure the translational invariance of the total Hamiltonian. The part

$$H_{\mathrm{S}\alpha} = Y^\alpha \otimes B^\alpha, \qquad (4)$$

is the system-bath coupling Hamiltonian, wherein B^α denotes the collective bath operator. For notational ease throughout this work we will set $\hbar = 1$ and $k_{\mathrm{B}} = 1$. In general, the above Hamiltonian permits transport in the presence of a temperature difference among the baths.

Given the above Hamiltonian, we first derive an equation, similar to the time-local Redfield quantum master equation [19], which helps us deduce the RDM of the system for such a nonequilibrium scenario. We start by the basic quantum mechanical definition of the *total* density matrix at any time t given by

$$\rho_{\mathrm{tot}}(t) = U(t)\rho_{\mathrm{tot}}(0)U(t)^\dagger, \qquad (5)$$

where $U(t) = \exp[-i\,H_{\mathrm{tot}}t]$ is the total time evolution operator. Assuming that each of the baths are weakly coupled to the system we may expand the total evolution operator up to second order to read

$$U(t) \approx e^{-i\,H_\mathrm{o}t} \left\{ \mathbb{I} - \sum_\alpha \left[i \int_0^t dq (\tilde{H}_{\mathrm{S}\alpha}(q) + \tilde{H}_{\mathrm{R}\alpha}(q)) \right. \right.$$
$$\left. \left. + \int_0^t dq\, \tilde{H}_{\mathrm{S}\alpha}(q) \int_0^q du\, \tilde{H}_{\mathrm{S}\alpha}(u) \right] \right\}, \qquad (6)$$

where $H_\mathrm{o} = H_{\mathrm{S}} + \sum_\alpha H_\alpha$ and all operators with $\sim$'s denote the Heisenberg evolution (also known as free evolution) under H_o, i.e., $\tilde{O}(x) = e^{i H_\mathrm{o}x} O\, e^{-i H_\mathrm{o}x}$.

Assuming that the system and the baths are decoupled initially, i.e., $\rho_{\mathrm{tot}}(0) = \rho_{\mathrm{S}}(0)\Pi_\alpha^\otimes \rho_\alpha(0)$, with each bath being in its canonical distribution, i.e., $\rho_\alpha(0) = \exp[-\beta^\alpha H_\alpha]/Z_\alpha$, and tracing over the bath degrees of freedom, we obtain

$$\frac{d\rho(t)}{dt} = -i\left[\left(H_{\mathrm{S}} + \sum_\alpha H_{\mathrm{R}\alpha} \right), \rho(t) \right] + \mathcal{R}(t), \qquad (7)$$

where $\rho(t)$ is the RDM of the system and $[\cdot,\cdot]$ is the commutator. The *relaxation* operator $\mathcal{R}$, which ensures that the system is damped by the baths, is given by

$$\mathcal{R}(t) = -\sum_\alpha \int_0^t dq \{ [Y^\alpha, \tilde{Y}^\alpha(q-t)\rho(t)]C^\alpha(t-q)$$
$$- [Y^\alpha, \rho(t)\tilde{Y}^\alpha(q-t)]C^\alpha(q-t) \}, \qquad (8)$$

where $C^\alpha(\tau) = \mathrm{Tr}_\alpha[\tilde{B}^\alpha(\tau)B^\alpha \rho_\alpha(0)]$ is the α-th bath correlator, where the trace is over the α-th bath. One might argue here that, mathematically, this average should be with respect to the 0-th order density matrix of the bath at time t. It is here we invoke the physical assumption that the bath is extremely large and cannot be influenced by the system. This leads the bath to remain in its initially prepared state, $\exp[-\beta^\alpha H_\alpha]/Z_\alpha$. The physical assumption, also commonly referred to as the Born approximation, implies that the bath-correlator follows a Kubo-Martin-Schwinger (KMS) condition [40,41], i.e., $C^\alpha(-\tau) = C^\alpha(\tau - i\,\beta^\alpha)$, and the transition rates $\mathrm{Re}[W_{kl}^\alpha]$ follow a detailed balance, i.e., $\mathrm{Re}[W_{kl}^\alpha] = \exp[-\beta^\alpha \Delta_{kl}]\mathrm{Re}[W_{lk}^\alpha]$. In the derivation above we have assumed $\mathrm{Tr}_\alpha[B^\alpha \rho_\alpha(0)] = 0$, but more generally the term of the form $-i \sum_\alpha [Y^\alpha, \rho(t)]\mathrm{Tr}_\alpha[B^\alpha \rho_\alpha(0)]$ must be added to the right-hand side of Eq. (7). It is important to note that the effects of multiple baths is additive in the *relaxation* operator $\mathcal{R}(t)$ because our total Hamiltonian did not contain any cross terms having bath-bath correlations.

Expressing the non-Markovian master equation Eq. (7) in the energy eigenbasis of the system Hamiltonian, we find

$$\frac{d\rho_{nm}(t)}{dt} = -i\,\Delta_{nm}\rho_{nm}(t) + \sum_{kl} \mathcal{R}_{nm}^{kl}\rho_{kl}(t), \qquad (9)$$

where $\Delta_{nm} = E_n - E_m$ is the difference in energies of the bare system Hamiltonian and the relaxation four tensor $\mathcal{R}_{nm}^{kl}$, which captures the non-Markovian nature, is given by

$$\mathcal{R}_{nm}^{kl} = \sum_\alpha \left[Y_{nk}^\alpha Y_{lm}^\alpha \left(W_{nk}^\alpha + W_{ml}^{\alpha*} \right) - \delta_{l,m} \sum_j Y_{nj}^\alpha Y_{jk}^\alpha W_{jk}^\alpha \right.$$
$$\left. - \delta_{n,k} \sum_j Y_{lj}^\alpha Y_{jm}^\alpha W_{jl}^{\alpha*} \right]. \qquad (10)$$

The rates W_{kl}^α take the form

$$W_{kl}^\alpha = \tilde{W}_{kl}^\alpha + i\,\frac{\gamma_0^\alpha}{2}, \qquad (11)$$

where

$$\tilde{W}_{kl}^\alpha = \int_0^t d\tau\, e^{-i\Delta_{kl}\tau}\, C^\alpha(\tau), \qquad (12)$$

$$\gamma_0^\alpha = \sum_{k=1}^\infty \frac{c_{k,\alpha}^2}{m_{k,\alpha}\,\omega_{k,\alpha}^2}. \qquad (13)$$

The damping kernel at zero time γ_0^α arises from the renormalization part of the Hamiltonian $H_{\mathrm{R}\alpha}$.

III. STEADY-STATE NONEQUILIBRIUM MODIFIED REDFIELD SOLUTION

The QME given in Eq. (7) is analogous to the Redfield master equation but here in the presence of multiple baths. Hence, similar to the Redfield case, the above equation also does not provide the correct steady-state solution [22–24] and contains errors in the diagonal terms of the RDM at the second order of system-bath coupling. To avoid these errors and to obtain the RDM correctly up to second order, in this section we employ the techniques of the modified Redfield solution [24] for the nontrivial nonequilibrium steady-state scenario.

A. Extracting the correct steady-state RDM elements from the quantum master equation

We start by extracting the correct steady-state elements of the RDM from the time-local Redfield-like QME Eq. (9). In order to establish a steady state we first take the limit $t \to \infty$ by setting the upper limit of the integral in Eq. (12) to ∞. The steady-state condition then implies

$$\frac{d\rho_{nm}(t)}{dt} = 0. \quad (14)$$

Since we assumed a weak system-bath coupling approximation while deriving the time-local Redfield-like QME, we consistently do the same in case of the steady-state RDM ρ_{nm} and assume a general power series expansion in the coupling strength of the form

$$\rho_{nm} = \sum_{i=0,2,4,\cdots} \rho_{nm}^{(i)}. \quad (15)$$

Above, $\rho^{(i)}$ is the i-th order RDM, where i indicates the power dependence of the system-bath coupling. The $\rho_{nm}^{(0)}$ above should be interpreted as the RDM obtained in the limit the system-bath coupling goes to zero. The limit is crucial to ensure that the system, instead of staying in its initial state, feels the effect of the bath and relaxes to the correct steady state.

Similar to the equilibrium case [23,24], it can be shown that the steady-state diagonal elements obtained by solving Eq. (9) are incorrect in the second order of system-bath coupling. Hence, using Eq. (15) in Eq. (9) and solving order by order, we obtain the 0-th order elements as

$$\sum_{\alpha,k} \left(Y_{nk}^\alpha Y_{kn}^\alpha \tilde{W}_{nk}^{\alpha\prime} - \delta_{n,k} \sum_l Y_{nl}^\alpha Y_{lk}^\alpha \tilde{W}_{lk}^{\alpha\prime} \right) \rho_{kk}^{(0)} = 0, \quad (16)$$

while for ($n \neq m$),

$$\rho_{nm}^{(0)} = 0, \quad (17)$$

where $\tilde{W}_{kl}^{\alpha\prime} = \mathrm{Re}[\tilde{W}_{kl}^\alpha]$. Unlike the equilibrium case, the solution to the above is in general not a Gibbs-distribution due to the lack of a detailed balance condition. The second-order off-diagonal elements are given by

$$\rho_{nm}^{(2)} = \frac{1}{i\,\Delta_{nm}} \sum_{\alpha,k} Y_{nk}^\alpha Y_{km}^\alpha \left[\left(W_{nk}^\alpha + W_{mk}^{\alpha*} \right) \rho_{kk}^{(0)} \right.$$
$$\left. - W_{kn}^{\alpha*} \rho_{nn}^{(0)} - W_{km}^\alpha \rho_{mm}^{(0)} \right], \quad (n \neq m). \quad (18)$$

The above set of equations describing the 0-th order and second-order off-diagonal elements have been obtained under the assumption that our *bare* system Hamiltonian does not possess any degeneracies in its energy eigenspectrum. The 0-th order equation, Eq. (17), can also be equivalently obtained in the van Hove limit (also sometimes referred to as the Davies limit [20,42]) by rescaling the time t and coupling strength λ as $\lambda t = \tau$, where τ should always remain constant [43]. In the steady state, since $t \to \infty$, the coupling obeys $\lambda \to 0$ so τ remains constant. This causes the second-order off-diagonal elements to vanish in the steady state and, hence, we make use of the time-local Redfield-like QME which retains some of the crucial second-order information.

B. Analytic continuation to obtain second-order diagonal elements

Following the same reasoning used in our previous work [24], in this section we obtain the second-order diagonal elements of the steady-state nonequilibrium RDM. In order to do this we make use of analytic continuation techniques and use only the information provided by a second-order time-local Redfield-like QME Eq. (9). We start by a careful inspection of the second-order off-diagonal elements [Eq. (18)] and assume that the energy E_m continuously approaches E_n by a small complex parameter z, i.e., $E_m = E_n - z$, yielding

$$\rho_{nn}^{(2)} \propto \lim_{z \to 0} \left\{ \frac{1}{i\,z} \sum_{\alpha,k} Y_{nk}^\alpha Y_{kn}^\alpha \left[\left(\tilde{W}_{nk}^{\alpha\prime}(0) + \tilde{W}_{nk}^{\alpha\prime}(-z) \right) \rho_{kk}^{(0)} - \left(\tilde{W}_{kn}^{\alpha\prime}(0) + \tilde{W}_{kn}^{\alpha\prime}(z) \right) \rho_{nn}^{(0)} \right] \right.$$
$$\left. + \frac{1}{z} \sum_{\alpha,k} Y_{nk}^\alpha Y_{kn}^\alpha \left[\left(\tilde{W}_{nk}^{\alpha\prime\prime}(0) - \tilde{W}_{nk}^{\alpha\prime\prime}(-z) \right) \rho_{kk}^{(0)} - \left(\tilde{W}_{kn}^{\alpha\prime\prime}(0) - \tilde{W}_{kn}^{\alpha\prime\prime}(-z) \right) \rho_{nn}^{(0)} + \left(\tilde{W}_{kn}^{\alpha\prime\prime}(-z) + \frac{\gamma_0}{2} \right) z \frac{\partial \rho_{nn}^{(0)}}{\partial E_n} \right] \right\}, \quad (19)$$

where

$$\tilde{W}_{kl}^\alpha(z) = \int_0^\infty d\tau\, e^{-i\,(\Delta_{kl}+z)\tau}\, C^\alpha(\tau), \quad (20)$$

$\tilde{W}_{kl}^{\alpha\prime}(z) = \mathrm{Re}[\tilde{W}_{kl}^\alpha(z)]$, and $\tilde{W}_{kl}^{\alpha\prime\prime}(z) = \mathrm{Im}[\tilde{W}_{kl}^\alpha(z)]$. Above, since $\rho_{mm}^{(0)}$ also depends on the energy E_m, we made use of the Taylor expansion of $\rho_{mm}^{(0)}$ of the form

$$\lim_{E_m \to E_n} \rho_{mm}^{(0)} \simeq \rho_{nn}^{(0)} + z \frac{\partial \rho_{nn}^{(0)}}{\partial E_n}. \quad (21)$$

Noting that $\lim_{z \to 0} \tilde{W}_{kl}^\alpha(z) = \tilde{W}_{kl}^\alpha(-z) = \tilde{W}_{kl}^\alpha$, we find

$$\rho_{nn}^{(2)} \propto \sum_{\alpha,k} Y_{nk}^\alpha Y_{kn}^\alpha \left[V_{nk}^{\alpha\prime\prime} \rho_{kk}^{(0)} - V_{kn}^{\alpha\prime\prime} \rho_{nn}^{(0)} \right] + W_{kn}^{\alpha\prime\prime} \frac{\partial \rho_{nn}^{(0)}}{\partial E_n}, \quad (22)$$

where

$$V_{kl}^{\alpha\prime\prime} = \frac{\partial \tilde{W}_{kl}^{\alpha\prime\prime}}{\partial \Delta_{kl}} = \lim_{z \to 0} \frac{\tilde{W}_{kl}^{\alpha\prime\prime}(0) - \tilde{W}_{kl}^{\alpha\prime\prime}(-z)}{z}, \quad (23)$$

$W_{kl}^{\alpha\prime\prime} = \mathrm{Im}[W_{kl}^\alpha]$, and $\tilde{W}_{kl}^{\alpha\prime\prime} = \mathrm{Im}[\tilde{W}_{kl}^\alpha]$. In order to obtain Eq. (22) we have omitted one of the terms which takes the same form as the left-hand side of Eq. (16) but is zero in the

limit $z \to 0$. The limiting procedure above is independent of the way in which E_m approaches E_n, implying the uniqueness of the limit and thus physically the steady state.

A reader might have observed the proportionality signs in Eqs. (19) and (22). This is mainly because the diagonal elements of the RDM have an additional constraint of normalization. At the 0-th order the trace should be unity, which immediately implies that the second-order elements should be traceless. Equation (22) does not preserve this normalization condition, due to the analytic continuity procedure. Therefore, we renormalize the RDM using

$$\rho_{nn} = \frac{\rho_{nn}^{(0)} + \rho_{nn}^{(2)}}{\sum_k \left(\rho_{kk}^{(0)} + \rho_{kk}^{(2)} \right)}$$
$$\simeq \rho_{nn}^{(0)} + \rho_{nn}^{(2)} - \rho_{nn}^{(0)} \sum_k \rho_{kk}^{(2)}, \qquad (24)$$

where we have ignored the fourth- and higher order terms and used the condition $\sum_k \rho_{kk}^{(0)} = 1$. Therefore, after this normalization, Eq. (22) transforms into

$$\rho_{nn}^{(2)} = \sum_{\alpha,k} Y_{nk}^{\alpha} Y_{kn}^{\alpha} \left[V_{nk}^{\alpha''} \rho_{kk}^{(0)} - V_{kn}^{\alpha''} \rho_{nn}^{(0)} + W_{kn}^{\alpha''} \frac{\partial \rho_{nn}^{(0)}}{\partial E_n} \right]$$
$$- \rho_{nn}^{(0)} \sum_{\alpha,k,l} Y_{lk}^{\alpha} Y_{kl}^{\alpha} W_{kl}^{\alpha''} \frac{\partial \rho_{ll}^{(0)}}{\partial E_l}, \qquad (25)$$

where $\partial \rho_{nn}^{(0)} / \partial E_n$ can be obtained by differentiating Eq. (16) as

$$\frac{\partial \rho_{nn}^{(0)}}{\partial E_n} = \frac{\sum_{\alpha,k \neq n} Y_{nk}^{\alpha} Y_{kn}^{\alpha} \left(V_{nk}^{\alpha'} \rho_{kk}^{(0)} + V_{kn}^{\alpha'} \rho_{nn}^{(0)} \right)}{\sum_{\alpha,k \neq n} Y_{nk}^{\alpha} Y_{kn}^{\alpha} \tilde{W}_{kn}^{\alpha'}}, \qquad (26)$$

where $V_{kl}^{\alpha'} = \partial \tilde{W}_{kl}^{\alpha'} / \partial \Delta_{kl}$. The above second-order diagonal elements constitute the main result of this paper. If we compare the above result to the equilibrium case [24], we find that the only difference amounts to an extra summation index α. This is obvious in hindsight because our initial model did not have any bath-bath correlations. Thus, Eqs. (16), (17), (18), and (25) form our nonequilibrium modified Redfield solution, which represents the RDM correctly up to second order in the system-bath coupling strength.

Although for a general system one needs to solve Eq. (16) using numerical techniques, we would like to point out one special regime where we may be able to obtain the solution analytically. Let us consider the regime where the temperature differences are small and identical baths with different temperatures are connected to a single system degree of freedom, i.e., $Y^{\alpha} = Y$ for all α. In this special regime an approximate Gibbs-distribution-like state exists for the 0-th order RDM, i.e., $\rho^{(0)} \approx \exp(-\bar{\beta} H_S)/\mathrm{Tr}_S[\exp(-\bar{\beta} H_S)]$, where $\bar{\beta}$ is the inverse of the arithmetic average temperature of various baths. Such a solution allows us to obtain the second-order RDM analytically, since the second-order terms are expressions which depend on $\rho^{(0)}$; refer to Eqs. (18) and (25). The existence of approximate Gibbs distributions have been investigated before for various classical models [44] and are valid in the quantum regime as long as the energy spectrum has a finite width. The width of the spectrum plays an important role and the narrower the energy spectrum the wider the regime

of validity of the approximate Gibbs state (for more information see the appendix). Although such a simple manifestation is true for the 0-th order RDM the statement cannot be extended to higher orders in terms of the generalized Gibbs distribution, i.e., $\rho \neq \mathrm{Tr}_B[\exp(-\bar{\beta} H_{\mathrm{tot}})]/\mathrm{Tr}[\exp(-\bar{\beta} H_{\mathrm{tot}})]$.

IV. CORROBORATION AND COMPARISON FOR THE QUANTUM HARMONIC OSCILLATOR

In this section we compare our nonequilibrium modified Redfield solution to the lone exact result of the quantum harmonic oscillator obtained via techniques of nonequilibrium Green's function [31]. For this specific case we will choose our system Hamiltonian to take the form

$$H_S = \frac{p^2}{2M} + \frac{1}{2} M \omega_0^2 x^2, \qquad (27)$$

where x, p, M, and ω_0 are the position, momentum, mass, and angular frequency of the oscillator, respectively. The harmonic oscillator poses a tough numerical challenge for traditional QMEs like Eq. (9) because of the relaxation four tensor $\mathcal{R}_{nm}^{kl}$ which scales as N^4, where N is the system Hilbert space dimension. The memory requirement for these traditional QMEs with a modest $N = 40$ is approximately 40 MB for storing only the relaxation tensor $\mathcal{R}_{nm}^{kl}$. Since our technique does not need to store the relaxation tensor and only relies on the storage of the rates W_{kl}^{α}, which scale as N^2, the memory requirement drastically drops to a mere 25 kB. This enables us to deal with large system Hilbert spaces like that of the harmonic oscillator. Also *uncontrolled* approximations like the rotating wave approximation [9] should not be applied to this model because of the equispaced energy spectrum, making this example a viable testing ground.

We then couple the harmonic oscillator linearly to the minimal transport setup involving two baths ($\alpha = $ L,R) via the position coupling, i.e., $Y^{L,R} = x$ and $B^{\alpha} = -\sum_{k=1}^{\infty} c_{k,\alpha} x_{k,\alpha}$ in Eq. (4). In order to describe the baths we will make use of the spectral density $J^{\alpha}(\omega)$ defined as

$$J^{\alpha}(\omega) = \pi \sum_{k=1}^{\infty} \frac{c_{k,\alpha}^2}{2 m_{k,\alpha} \omega_{k,\alpha}} \delta(\omega - \omega_{k,\alpha}). \qquad (28)$$

Now we will choose both baths to have same parameters, i.e., $J^L(\omega) = J^R(\omega) = J(\omega)$, which we will choose to be of the form

$$J(\omega) = \frac{M \gamma \omega}{1 + (\omega/\omega_D)^2}. \qquad (29)$$

The above form of the spectral density is known as the Lorentz-Drude form, where ω_D denotes the cut-off frequency and $\gamma \propto \sum_{k=1}^{\infty} c_k^2$ is the phenomenological Stokesian damping coefficient which characterizes the system-bath coupling strength.

Using this definition of spectral density we can now recast the bath correlator $C^{\alpha}(\tau)$ as

$$C^{\alpha}(\tau) = \int_0^{\infty} \frac{d\omega}{\pi} J(\omega) \left[\coth\left(\frac{\beta^{\alpha} \omega}{2} \right) \cos(\omega\tau) - i \sin(\omega\tau) \right]. \qquad (30)$$

For the given Lorentz-Drude model the bath correlator can be evaluated analytically and it takes the form

$$C^\alpha(\tau) = \frac{M\gamma}{2}\omega_D^2\, e^{-\omega_D\tau}\left[\cot\left(\frac{\beta^\alpha\omega_D}{2}\right) - i\,\mathrm{sgn}(\tau)\right]$$
$$- \frac{2M\gamma}{\beta^\alpha}\sum_{j=1}^{\infty}\frac{\nu_j^\alpha\, e^{-\nu_j^\alpha\tau}}{1-\left(\nu_j^\alpha/\omega_D\right)^2}, \tag{31}$$

where $\nu_j^\alpha = 2\pi j/\beta^\alpha$ are known at the Matsubara frequencies. The damping kernel defined in Eq. (13) can also be written in terms of $J(\omega)$ as

$$\gamma_0^L = \gamma_0^R = \gamma_0 = \frac{2}{\pi}\int_0^\infty d\omega\,\frac{J(\omega)}{\omega}, \tag{32}$$

and for the Lorentz-Drude model as $\gamma_0 = \gamma\omega_D$.

Therefore, the components of the rates $\tilde{W}^\alpha$, defined in Eq. (12), read as follows:

$$\tilde{W}_{kl}^{\alpha\prime} = J(\Delta_{kl})\,n^\alpha(\Delta_{kl}), \tag{33}$$

$$\tilde{W}_{kl}^{\alpha\prime\prime} = \frac{M\gamma\omega_D^2\Delta_{lk}}{2(\omega_D^2+\Delta_{kl}^2)}\left[\cot\left(\frac{\beta^\alpha\omega_D}{2}\right) + \frac{\omega_D}{\Delta_{kl}}\right]$$
$$+ \frac{2M\gamma}{\Delta_{kl}\beta^\alpha}\sum_{j=1}^{\infty}\frac{\nu_j^\alpha}{\left(1-\left(\nu_j^\alpha/\omega_D\right)^2\right)\left(1+\left(\nu_j^\alpha/\Delta_{kl}\right)^2\right)}, \tag{34}$$

where the Bose-Einstein distribution function $n^\alpha(\Delta_{kl}) = [\exp(\beta^\alpha\Delta_{kl})-1]^{-1}$, with the inverse temperature β^α for each bath.

Now once we have defined the bath properties and the coupling to the system, we calculate the nonequilibrium modified Redfield solution for the harmonic oscillator problem using a fixed number of energy levels. We truncate the number of levels by ensuring that the highest few are unoccupied up to temperatures of $5\times T_D$, with $T_D = (\hbar\omega_0)/k_B$ being the Debye temperature. This results in the use of ≈ 40 energy levels for the single quantum harmonic oscillator. In order to corroborate with the exact nonequilibrium Green's function (NEGF) results of Dhar *et al.* [31], we define a discrepancy error,

$$D_{kl}^X \equiv \frac{\rho_{kl}^{NEGF} - \rho_{kl}^X}{(\gamma/\omega_0)}, \tag{35}$$

where ρ^{NEGF} describes the exact RDM obtained via the NEGF method and ρ^X could be the RDM either from the nonequilibrium modified Redfield solution (X = NMRS) or the time-local Redfield-like quantum master equation (X = TLQME) described in Sec. II. Now, because the second-order RDM, i.e., $\rho^{(2)}$, is proportional to γ it is clear that if ρ^{NEGF} matches ρ^X up to second order, then the discrepancy error $D^X \to 0$ as $\gamma \to 0$. In other words, ρ^{NEGF} matches ρ^X in the first order of dissipation strength γ (second order of coupling strength) for an arbitrary value of dissipation only if $D^X \to 0$ as $\gamma \to 0$ is obeyed.

In Fig. 1 we depict the discrepancy error D_{11}^X in the first level population of the RDM. Since the temperatures of the baths are kept low, the first level populations depict a fair representation of the entire RDM. Clearly, the discrepancy error shows the correct behavior only for the NMRS [Fig. 1 (top)], whereas for the TLQME [Fig. 1 (bottom)] as $\gamma \to 0$ the discrepancy error goes to a constant. This indicates that
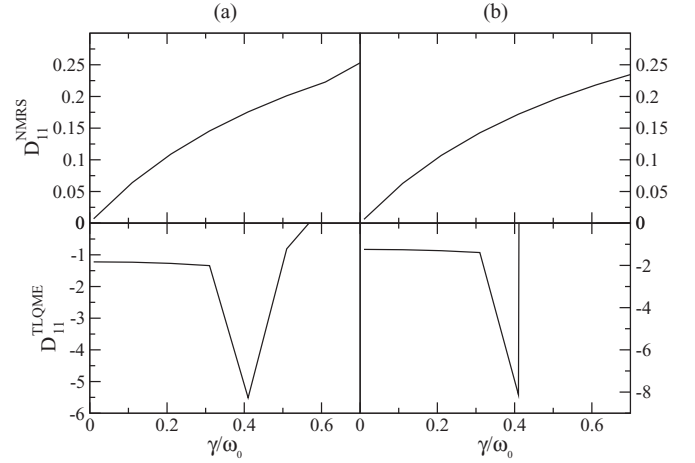

FIG. 1. Plot of the discrepancy error D_{11}^X, see Eq. (35), of the ground-state population versus the dimensionless system-bath coupling strength (γ/ω_0) for a quantum harmonic oscillator connected to two heat baths. The top panel shows the discrepancy error for the nonequilibrium modified Redfield solution ($X = $ NMRS) and the bottom panel is for the time-local Redfield-like quantum master equation ($X = $ TLQME). Panel (a) is for temperatures $T_L = 156$ K and $T_R = 140$ K, whereas panel (b) is for $T_L = 156$ K and $T_R = 78$ K. Other parameters used for the calculation are $M = 1$ u, $\omega_0 = 1.3\times10^{14}$ Hz, and $\omega_D = 10\omega_0$.

the TLQME contains errors in the second order of the RDM. These errors in nonequilibrium can lead to inaccurate results, especially when one tries to calculate the current based on the local operator definition. Thus it is only the NMRS which is well suited for such applications since it accurately captures all system-bath coupling effects to the lowest order. Importantly, the bath temperatures do not play a major role in Fig. 1 and the same qualitative behavior is observed for all temperature ranges and differences.

Next, in Fig. 2, we compare our NMRS to the TLQME, the Lindblad-like master equation [8,21,45], and the exact NEGF results [31]. The Lindblad-like solution (dashed green line) is (completely) positive, which has been critiqued before for a system connected to a single bath [46–48], and it fails to capture the effects of the finite system-bath coupling. These erroneous behaviors of the Lindblad-like solution could present a serious drawback to tackle transport problems where the dependence on coupling strength is of primal importance. On the other hand, the TLQME (dash-dotted red line) produces unphysical negative probabilities, even for moderate coupling strengths [Fig. 2 (middle panel) $\gamma/\omega_0 = 0.25$ and (bottom panel) $\gamma/\omega_0 = 0.5$]. In the equilibrium case this problem has been critiqued repeatedly [49,50], but to the best of our knowledge the issue has not been addressed in the nonequilibrium scenario. Clearly, the breaking of positivity for the TLQME is a result of incorrect second-order diagonal elements, because our NMRS (solid blue line) seems to behave reasonably well for coupling strengths well beyond the naive expectation for a perturbative master equation. Also, as compared to the exact NEGF results (maroon stars), which take into account all orders of coupling strength, our NMRS result shows excellent agreement, even in the moderate coupling strength regime, i.e., for $\gamma/\omega_0 = 0.25$ and $\gamma/\omega_0 = 0.5$. In this moderate coupling
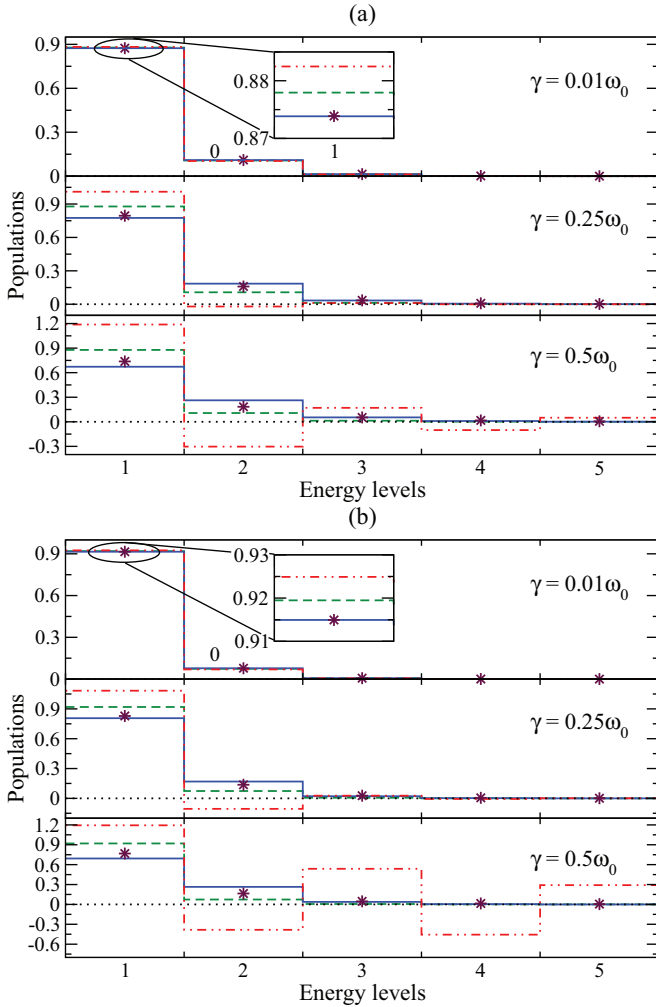
FIG. 2. (Color online) Histogram of the populations for the first five lowest-lying energy levels for different system-bath coupling strengths for a damped quantum harmonic oscillator. Panel (a) corresponds to $T_L = 312$ K, $T_R = 280.8$ K and panel (b) to $T_L = 312$ K, $T_R = 156$ K. The inset in the top panels is a zoom of the first energy level populations. The solid (blue) lines correspond to our nonequilibrium modified Redfield solution (NMRS), the dash-dotted (red) lines present the results for the time-local Redfield-like quantum master equation (TLQME), the dashed (green) lines depict the results for the Lindblad-like solution, and the (maroon) stars represent the exact NEGF results. The parameters used for the calculation are $M = 1$ u, $\omega_0 = 1.3 \times 10^{14}$ Hz, and $\omega_D = 10\omega_0$.

strength regime it is expected that higher orders of the coupling strength will also play a role, due to which a small difference is observed between the exact NEGF results and our second-order NMRS approach. It should also be noted that the NMRS is not (completely) positive and can even give rise to negative populations if the coupling strength increases far beyond its *a priori* regime of validity of finite weak coupling. The qualitative features of the results described above do not depend on temperature differences [as seen from Figs. 2(a) and 2(b)] or on absolute temperature, implying that our NMRS is an excellent method to accurately capture nonequilibrium effects in the weak to moderate system-bath coupling regimes.

V. CONCLUDING REMARKS AND FUTURE DIRECTIONS

In summary, we presented a novel technique based on analytic continuity to evaluate the steady-state reduced density matrix of a general anharmonic system connected to multiple heat baths correct up to second order in the system-bath coupling. Our novel NMRS was verified against the only known exact nonequilibrium solution of the quantum harmonic oscillator and excellent agreement is obtained between these two approaches. Other "popular" quantum master equations were then compared against our NMRS and considerable differences were found in the regime of moderate system-bath coupling. In this regime, it was only the NMRS that provides physically reliable solutions, whereas the other approaches either violated positivity or did not change with increasing coupling strength. In order to study systems in nonequilibrium the moderate (or at least weak but finite) coupling strength regime is extremely crucial because some of the most interesting phenomena, like transport, solely depend on the strength of the coupling and are trivially zero for vanishing couplings. Thus, in cases where local current operators are defined, our NMRS presents an accurate nonphenomenological approach to deal with steady-state transport.

Even though our approach is accurate and numerically efficient, several unresolved challenges still remain. One subtle issue lies in dealing with systems which posses a degeneracy for the eigenvalues in the bare system Hamiltonian. One can mathematically circumvent this issue by recalculating the order-by-order solution for degenerate systems, as done in Sec. III A for the case of nondegenerate systems, and then use our analytic continuity approach to tackle the second-order diagonal elements correctly. Another important challenge lies in the hierarchical nature of the master equations, i.e., in order to know the n-th order RDM one requires a $n + 2$-th order master equation. Our novel approach has demonstrated that up to second order there is a reasonable route to bypass this hierarchical problem and work at a given order, but it is still an open question if such a scheme would even work for higher orders. A deeper mathematical or physical understanding of why the analytic continuation works is also not settled. It is also not clear how one could extend our scheme to study the relaxation dynamics. The uniqueness of the steady state makes our approach feasible, but the dynamical problem is a herculean task because there could be various equivalent dynamical routes. Despite its limitation to steady state we are confident that our approach paves a new way to address nonequilibrium physics in general anharmonic systems beyond the vanishing coupling limit.

APPENDIX: APPROXIMATE GIBBS DISTRIBUTION IN THE LIMIT OF VANISHING COUPLING

In specific parameter regimes it is possible to approximate the 0-th order RDM, described in the main body of the paper, as an effective canonical distribution $\rho^{(0)} \approx e^{-\bar{\beta}H_S} / \text{Tr}_S[e^{-\bar{\beta}H_S}]$,

with an effective inverse temperature. Here, we would like to numerically illustrate this idea using a simple example of a system connected to two identical harmonic heat baths, with different temperatures, denoted by "L" (left bath) and "R" (right bath). We look at the equation describing the 0-th order RDM, Eq. (16), and limit our investigation to the regime where both the baths are connected to the same system operator, i.e., $Y^L = Y^R = Y$. Therefore Eq. (16) can be recast as

$$\sum_k \left(Y_{nk} Y_{kn} \tilde{W}_{nk}^{c'} - \delta_{n,k} \sum_l Y_{nl} Y_{lk} \tilde{W}_{lk}^{c'} \right) \rho_{kk}^{(0)} = 0, \qquad (A1)$$

where $\tilde{W}^{c'} = \tilde{W}^{L'} + \tilde{W}^{R'}$. Equation (A1) resembles an approximate detailed balance equation if the rates $\tilde{W}^{c'}$ follow

$$\tilde{W}_{ij}^{c'} \approx \exp(-\bar{\beta} \Delta_{ij}) \tilde{W}_{ji}^{c'}, \qquad (A2)$$

where $\Delta_{ij} = E_i - E_j$ is the energy difference of the system Hamiltonian and $\bar{\beta} = 2\beta^L \beta^R / (\beta^L + \beta^R)$ represents the inverse of the average temperature. Now since both the baths have the same physical properties, i.e., $J^L(\omega) = J^R(\omega) = J(\omega)$, then using Eq. (33) from the main text, which in fact is true for all spectral densities, it can be shown that Eq. (A2) is equivalent to

$$\chi(\Delta_{ij}, \beta^L, \beta^R) = \ln \left[\frac{e^{\beta^L \Delta_{ij}} + e^{\beta^R \Delta_{ij}} - 2}{2 e^{(\beta^L + \beta^R)\Delta_{ij}} - e^{\beta^L \Delta_{ij}} - e^{\beta^R \Delta_{ij}}} \right]$$
$$+ \bar{\beta} \Delta_{ij} = 0. \qquad (A3)$$

Thus, without the need of defining a system Hamiltonian or the bath properties it is possible to numerically check the validity of Eq. (A3) for various energy differences and
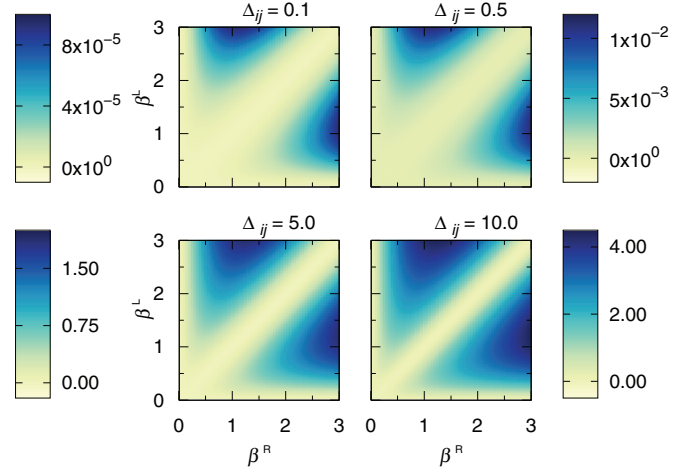

FIG. 3. (Color online) Plot of the $\chi(\Delta_{ij}, \beta^L, \beta^R)$ as a function of inverse temperatures of the baths β^L and β^R for different energy differences Δ_{ij}.

temperatures as shown in Fig. 3. Clearly, when $\beta^L \approx \beta^R$, i.e., slightly off the diagonals of Fig. 3, Eq. (A3) is satisfied to a large extent. In cases where the energy difference of the system Hamiltonian is not that large the regime of validity of the approximate detailed balance condition goes well beyond the small temperature-difference regime. Keeping in mind that the Eq. (A3) should be valid for all combinations of energy differences, we infer that the approximate Gibbs behavior, beyond the trivial small temperature-difference regime, is applicable for systems whose width of the energy spectrum is much smaller than the temperatures of the baths.

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