

Efficient energy resolved quantum master equation for transport calculations in large strongly correlated systems

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We introduce a systematic approximation for a more efficient evaluation of the Born–Markov master equation (BMME) for steady state transport studies in open quantum systems out of equilibrium: the energy resolved master equation approach (ERMEA). The master equation is formulated in the eigenbasis of the system and build successively by inclusion of eigenstates with rising eigenenergies. In order to quantify convergence of the approximately built superoperator we introduce quality factors to check preservation of trace, positivity and hermiticity. In order to avoid the commonly used secular approximation, we furthermore introduce a symmetrized BMME which allows to treat quasi-degenerate states correctly and leads to a master equation of Lindblad form which reproduces the secular limit. The here presented improvements are benchmarked for a six orbital quantum system which shows destructive quantum interference in non-equilibrium. ERMEA shows that quantum transport calculations in quantum systems also beyond six orbitals are accessible in a numerically efficient and stable way.

I. INTRODUCTION

In the breakdown of Moore’s law when reaching the quantum limit, the study of quantum effects on electronic transport is becoming increasingly important. The quantum nature of electrons is not only a source of error for logical circuits, but also opens up a wide range of new applications, provided that one is able to correctly predict, understand and enhance the quantum effects, which mostly arise at small scales and low temperatures. One of the most successful methods to derive an appropriate description of the electronic landscape for such systems in that parameter regime is the non-equilibrium density functional theory (DFT) in combination with non-equilibrium Green function (NEGF) techniques [1, 2]. However, their mean-field nature and the diagrammatic difficulties in the calculation of the correction term (self-energy) have major disadvantages when investigating transport effects arising in a system of strongly correlated electrons.

Therefore the concept of a so-called open quantum system is used which in principle describes a finite strongly correlated quantum system under the influence of a large environment that determines the actual state of the quantum system. In order to study transport in open quantum systems an effective differential equation (master equation [3]) and effective time evolution (dynamical map) have to be derived.

Whereas recent developments of quantum master equations such as hierarchical quantum master equation [4, 5] or auxiliary master equation [6, 7] concentrate on single or double impurities, the focus of this work is to tackle systems with a rather large number of orbitals to allow for rich quantum interactions. With increasing

number of included degrees of freedom N in the system it becomes exponentially hard to derive an effective dynamical map (called master equation in its differential form). The size of the density operator scales with 4^N whereas the size of the superoperator of the time evolution scales with the squared size of the density operator [8]. To climb this exponential wall (4^{2N}) we introduce the so-called energy resolved master equation approach (ERMEA), which provides a systematic approximation of the searched superoperator (also referred to as generator of a dynamical map) in the energy states that are relevant for the dynamics. ERMEA makes master equation techniques applicable to larger ab-initio derived strongly correlated quantum systems including baths with multiple orbitals described by Green functions representing arbitrary density of states.

In order to validate this approximation of the superoperator we introduce quality factors, which measure properties of the superoperator action on the density operator such as preservation of trace, preservation of hermiticity and positivity to verify convergence of the approximation.

This energy resolved approach is applicable to Markovian and non-Markovian types of master equations. For demonstration reasons we limit our discussion in this paper to the Born–Markov master equation (BMME) which is well apt to derive the steady state properties of open quantum system in the weak coupling regime.

a. Avoiding the secular approximation: There are various types of BMME. One very common type uses the **secular approximation**, which states that no coherences between system eigenstates of different energy will occur [9]. This approximation works well for systems with a clearly separated eigenspectrum in weak coupling. We refer to this type of BMME as **type A**. The big advantage of the secular approximation in this case is that the BMME can be cast into Lindblad form which – for the such derived universal dynamical map – guarantees

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positivity [10].

Because the model parameters for real material applications are derived from numerical DFT calculations, the system under investigation does not necessarily fulfill the requirements for the widely used secular approximation, since quasi-degenerate low energy states can occur and thus makes conventional derivations of master equations using Born–Markov–Secular approximation unsuitable. One solution is to derive a BMME without the secular approximation [11, App. A] which has the disadvantage that it cannot be reduced to Lindblad form, we refer to this as **type B**.

To mitigate this dilemma (Lindblad form combined with a clear statement about positivity on the one hand and correct description of the dynamics of quasi-degenerate states on the other), we introduce a symmetrized form of the BMME called **type C** which takes correlations of states with different eigenenergies into account and also leads to a Lindblad form which under certain conditions preserves positivity. We show that this type C master equation reproduces the Lindblad form (type A) in the secular limit. Tab. I summarizes the three types of BMME described in this paper.

TABLE I. Used BMME and their properties. We introduce type C to enhance the treatment of quasi-degenerate eigenstates in a Lindblad form.

Type	Uses secular approximation	Lindblad form	Preserves positivity	Eq.
A	yes	yes	yes	(4) & (D4)
B	no	no	often	(6)
C	no	yes	often	(23)

The article is structured as follows:

In Sec. II we summarize the theory of dynamical maps, shortly illustrate the microscopic derivation of the BMME for a fermionic system and introduce the ER-MEA. Furthermore the convergence parameters for the qualification of the approximation are introduced.

In Sec. III we introduce the **symmetrized Born–Markov master equation** (type C) in order to circumvent the secular approximation and we show that we retain a Lindblad type form of a dynamical map.

Numerically results for ERMEA and BMME type C are discussed in Sec. IV.

Finally Sec. V gives a short summary and outlook of possible applications.

II. ENERGY RESOLVED MASTER EQUATION APPROACH

A. Dynamical map - the theory in a nutshell

For a profound introduction to the field of quantum dynamical maps, uniformly continuous semigroups and

quantum master equations please refer to the excellent review of Rivas and Huelga [12].

Given is an **open quantum system**, consisting of a quantum system of interest (S), a bath or environment (B) and a (weak) coupling (I) between both. The reduced density operator $\sigma(t)$ provides a full description for S in the open quantum system and can be obtained from the full density operator $\rho(t)$ by tracing out the bath degrees of freedom $\sigma(t) = \text{Tr}_B\{\rho(t)\}$ or by using a projection operator \mathcal{P} that projects on the states of interest $\sigma(t) = \mathcal{P}\rho(t)\mathcal{P}$.

In order to describe the dynamics of such a system under the influence of the baths an effective differential equation, in this context referred to as **quantum master equation**, of the following form is searched:

$$\frac{d\sigma(t)}{dt} = K(\rho_B(t), t)[\sigma(t)], \quad (1)$$

$$\sigma(t_0) = \sigma_0. \quad (2)$$

In general such a differential equation for some part of a quantum system does not always exist. Already present **correlations** between system and environment which cannot be reduced to a unitary time evolution of a tensor product at some initial time, make it impossible to derive a differential equation since the information of correlation is missing. If for a time t_0 the quantum system is in a product state $\rho(t_0) = \sigma(t_0) \otimes \rho_B(t_0)$ which corresponds to having no correlations between S and B , then a formulation of a quantum master equation for that time t_0 is possible.

The central part of this master equation is the **generator** $K(\rho_B(t), t)$ which is in general a time-dependent non-linear superoperator [13]. The solution $\mathcal{U}(t, t_0, \rho_B(t_0), \sigma(t_0))$ of the quantum master equation is called **dynamical map**, incorporates the influence of the bath and of memory effects and provides an effective time evolution for S :

$$\sigma(t_1) = \mathcal{U}(t_1, t_0, \rho_B(t_0), \sigma(t_0)) \sigma(t_0), \quad (3)$$

which is related to the full unitary time evolution via partial traces over the bath degrees of freedom

$$\sigma(t_1) = \text{Tr}_B\{\mathcal{U}(t_1, t_0)\rho(t_0)\}.$$

For a shorter notation we omit from now on the dependence on the bath in the dynamical map: $\mathcal{U}(t_1, t_0, \sigma(t_0))$. Fig. 1 compares the dynamical map induced by tracing out the baths to a full unitary time evolution \mathcal{U} and points to the relation it should fulfill. In general such an effective time evolution (dynamical map) shall fulfill the following conditions, namely:

- Con 1. Preserve the trace of the density operator,
- Con 2. Preserve the hermiticity of the density operator,
- Con 3. Preserve the positivity of the density operator,

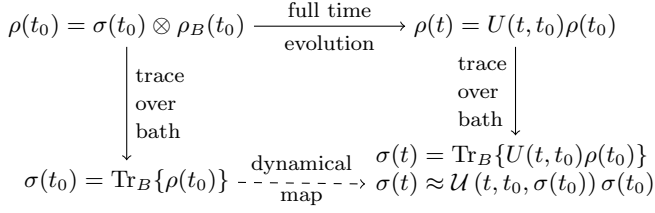


FIG. 1. Comparison of a trace-induced dynamical map to the full time evolution.

Con 4. Transitive / decomposition property:

$$\mathcal{U}(t_2, t_0, \sigma(t_0)) = \mathcal{U}(t_2, t_1, \sigma(t_1)) \circ \mathcal{U}(t_1, t_0, \sigma(t_0)).$$

In the following we will discuss which assumptions simplify the formulation of a dynamical with the listed properties.

a. Independence / linear generator: It is desirable to have a dynamical map $\mathcal{U}(t_1, t_0)$ which is independent from the initial density matrix and basically works for all start values $\sigma(t_0)$ [14]. It can be shown [12, Th. 4.3], that this holds true under the following condition, namely, that there is a time t_0 at which $\rho(t_0) = \sigma(t_0) \otimes \rho_B(t_0)$ can be written as a tensor product between system and bath (no quantum or classical correlations in the beginning) where the bath $\rho_B(t_0)$ is fixed for any $\sigma(t_0)$.

This independence from the initial value and applicability of the dynamical map on all initial states motivates the definition of a so called **universal dynamical map** (UDM), which requires besides Con. 1 and Con. 2 in addition complete positivity, which means $\mathcal{U}(t_1, t_0)\sigma(t_0)$ remains positive under any inclusion of a time evolution of the environment (it's positivity is compatible with any environment) [15].

b. Decomposition property: It is important to note that arising correlations between bath and system are an obstacle for the desired decomposition property (Con. 4) with UDMs. Assuming a tensor product as initial state at t_0 , a UDM can be formulated between $t_0 \rightarrow t_1$ and $t_0 \rightarrow t_2$. Because of the possible correlations it is per se not possible to have a UDM from $t_1 \rightarrow t_2$ [16]. The possible rise of correlations can sometimes be mitigated by a clever choice of what is the system and what is the bath so that both are only weakly coupled (weak coupling regime). In such a situation the so-called **Born approximation** is applicable which enforces the decomposition property by arguing that arising correlations between bath and system can be neglected ($\rho(t) \approx \sigma(t) \otimes \rho_B$), since the thermal bath is much larger compared to the coupling to the system so that every correlation immediately vanishes [17].

c. Steady state, time independence: In this work we are interested in the steady state properties of the system under investigation thus deal with a not only linear but also time-independent operator K in Eq. (1). As a consequence the searched effective time evolution operator

will only depend on a time difference

$$\sigma(t) = \mathcal{U}(t - t_0)\sigma(t_0) = e^{-iK(t-t_0)}\sigma(t_0).$$

The eigenvector of the linear operator K to the eigenvalue zero reveals the steady state properties of the system which will be the object of investigation in this work.

Having defined the general requirements of a UDM we now examine their implications on the form of a master equation. Demanding Con. 1 and Con. 2 to hold, leads consequently to the most general form of a universal dynamical map, the so-called Kossakowski–Lindblad equation [18, 19]:

LINDBLAD FORM
$\begin{aligned} \dot{\sigma}(t) = & -\frac{i}{\hbar}[H_S + H_{LS}, \sigma(t)] \\ & + \sum_{ij} \Gamma_{ij} \left(A_i \sigma(t) A_j^\dagger - \frac{1}{2} \{ A_j^\dagger A_i, \sigma(t) \} \right), \end{aligned} \quad (4)$ <p>with the full basis of trace-less operators A_i and the superindices $i \in [1, \dots, n^2 - 1]$ with the dimension n of the Hilbert space of the system (number of eigenstates). The matrix Γ incorporates the dissipative influence of the bath, whereas H_{LS} [20] represents a change for the system dynamics in comparison to the isolated system Hamiltonian H_S. Note that both terms Γ and H_{LS} vanish as the system–bath coupling goes to zero, thus retaining the von-Neumann equation of a closed quantum system.</p>

In order to fulfill Con. 3 we need the matrix Γ in Eq. (4) to be positive semidefinite [21].

After introducing the theoretical concept of a UDM which led to the Lindblad equation we now focus on how to derive the actual parameters from real physical models. There are various techniques to arrive at the Lindblad equation, one could derive the parameters from an ab-initio model (microscopic derivation) often using the Born–Markov approximation or some diagrammatic expansion, one could define the dissipation operators by fitting the bath hybridization function (auxiliary master equation approach [22]) or in optics one could engineer the coupling coefficients by varying the laser field which couples the system to an optical cavity [23].

In this paper we will follow roughly the first approach to demonstrate the concept of ERMEA.

B. Fermionic model and BMME, type B

The total Hamiltonian used for demonstration describes electronic transport and consists of three parts:

system, bath and coupling (perturbation) of system and bath:

$$H = H_S + H_B + H_I, \quad H_0 := H_S + H_B.$$

The finite system Hamiltonian H_S can be arbitrary. For simplistic reason it is chosen to be particle number and spin conserving. The bath Hamiltonian H_B is assumed to be solvable exactly and as such will be characterized by its bath Green function $G_{pl,\alpha}$. There can be more baths $\alpha = 1, 2, \dots$ with distinct thermodynamic properties such as temperature β_α and chemical potential μ_α which can consist of several different correlated orbitals p, l . Typical choices for the baths are non-interacting leads realized as semi-infinite tight binding chains or as flat bands in the wide band limit. The non-equilibrium situation of applying a bias voltage can be realized via shifting the chemical potentials in the baths or via shifting the densities of states. In this paper we stick to the first variant.

System and bath Hamiltonians together form the decoupled Hamiltonian denoted by H_0 .

The interaction Hamiltonian H_I is chosen in its most basic version, coupling a system degree of freedom to an eigenstate (in one orbital) of the baths,

$$\begin{aligned} H_I &= \sum_{\mu} c_{\mu}^{\dagger} \sum_{\alpha p} V_{\alpha p \mu} d_{p\alpha} + \text{h.c.} \\ &= \sum_{s\mu} s c_{\mu}^s \sum_{\alpha p} V_{\alpha p \mu}^s \bar{d}_{p\alpha}^{\bar{s}}, \\ s &\in \{-1, 1\}, \quad \bar{s} = -s, \quad c^s = \begin{cases} c & s = -1 \\ c^{\dagger} & s = +1 \end{cases}, \end{aligned} \quad (5)$$

and fulfills the condition that spin S and total particle number N (system and bath) remain preserved. $d_{p\alpha}, d_{p\alpha}^{\dagger}$ are the creation and annihilation operators of an electron on the first site of orbital p of bath α whereas $V_{\alpha p \mu}$ are the coupling constants.

As presented in literature one arrives (Born-Markov derivation in the weak coupling limit [10]) at the following equation:

BORN-MARKOV MASTER EQUATION, TYPE B

$$\begin{aligned} \dot{\sigma}(t) &= -i[H_S, \sigma(t)] \\ &\quad - \sum_{s\mu\kappa} [c_{\mu}^s, F_{\mu\kappa}^s(\mathcal{L}_S)\{c_{\kappa}^{\bar{s}}\}\sigma(t)] + \text{h.c.}, \end{aligned} \quad (6)$$

with the dissipators

$$F_{\mu\kappa}^s(\mathcal{L}_S) := \int_0^{\infty} d\tau C_{\mu\kappa}^s(\tau) e^{\mathcal{L}_S \tau}, \quad (7)$$

the bath correlation function

$$C_{\mu\kappa}^s(\tau) = \sum_{\alpha p l} V_{\alpha p \mu}^s \langle \bar{d}_{p\alpha}^{\bar{s}}(\tau) d_{l\alpha}^s \rangle V_{\alpha l \kappa}^{\bar{s}}, \quad (8)$$

and the Liouvillian superoperator $\mathcal{L}_S\{A\} := -i[H_S, A]$ [24]. In the notation used, the superoperator acts on all subsequent operators unless the effect is indicated by curly brackets as in Eq. (6). Using the eigenbasis $H_S|a\rangle = E_a|a\rangle$ we gain for the evaluation of a function f of the superoperator \mathcal{L}_S acting on the operator A the following rule

$$\langle a|f(\mathcal{L}_S)\{A\}|b\rangle = f(-i(E_a - E_b)) \langle a|A|b\rangle. \quad (9)$$

Eq. (6) is not yet in Lindblad form but allows a clearer representation for the arguments of the next subsection. The application of the secular approximation to arrive at type A master equation is illustrated in App. D. The master equation type C will be derived and discussed in Sec. III.

C. Energy resolved master equation

When using open quantum systems to determine steady state transport properties, there are two computationally very involved tasks: First the computation of the full superoperator itself and second the determination of the steady state by solving the eigenvalue problem given by the superoperator or by performing a time evolution with respect to the superoperator.

In this work we will introduce a physically motivated constructive way to represent the action of the superoperator in a small basis such that the determination of the steady state is possible without evaluating the full superoperator. This iterative construction of the representation of the superoperator is monitored using convergence parameters for trace (Con. 1), hermiticity (Con. 2) and positivity (Con. 3) which help to decide on when to stop the iteration. This provides a massive and systematic improvement on the calculability of steady states in the context of Lindblad equations.

As we show in Sec. IV reasonable effective representations of superoperators for six sites with this method can amount to a dimension of the order 10^3 compared to the Hilbert space of the full superoperator of the dimension 10^5 to 10^6 (compare Tab. II).

a. Motivation In an equilibrium situation (zero applied voltage V_B on the leads) the steady state of the weakly coupled system will be determined by the low energy states of the system Hamiltonian mostly [25]. The maximal applied difference in the chemical potential in the leads is in the range of some electronvolts since higher applied voltages would melt the leads. This energy range is rather small compared to the whole energy spectrum of a typical molecular system Hamiltonian which spans

several hundred electronvolts (see Fig. 3). Thus one can expect that the steady state non-equilibrium situation of the central system will not deviate a lot from the equilibrium state.

Therefore the basic idea of ERMEA is not to fully evaluate the master equation but successively derive an effective representation of the superoperator in the low energy eigenstates of the system Hamiltonian H_S . In order to make use of these considerations we formulate the master equation in the system eigenbasis, with eigenvectors $|a\rangle$ and eigenenergies E_a satisfying $H_S|a\rangle = E_a|a\rangle$.

This choice of the basis provides an advantage compared to other options, like the superfermion [26] notation which builds the superoperator in such a way as to adopt to creation and annihilation operators but not to the physical energy scale of the isolated system.

To outline this idea we define an energy cut \mathcal{E} and a projection operator \mathcal{P} on all eigenstates with corresponding lower eigenenergy

$$\mathcal{P} = \sum_{E_a < \mathcal{E}} |a\rangle\langle a|.$$

The orthogonal complement shall be denoted by $\mathcal{Q} = \mathbf{1} - \mathcal{P}$. For shorthand notation we split the reduced density operator in

$$\sigma = \begin{pmatrix} \sigma_{PP} & \sigma_{PQ} \\ \sigma_{QP} & \sigma_{QQ} \end{pmatrix},$$

with $\sigma_{PP} = \mathcal{P}\sigma(t)\mathcal{P}$, $\sigma_{PQ} = \mathcal{P}\sigma(t)\mathcal{Q}$, etc. For the effective representation of the superoperator we only take σ_{PP} into account and neglect the other terms of the density matrix which can be justified as follows:

Since the projection is onto eigenstates of the system Hamiltonian with different eigenenergies, the system Hamiltonian is block diagonal in the projection basis, e.g. $\mathcal{P}H_S\mathcal{Q} = 0$.

The master equation for the three different parts of the reduced density matrix are [27]

$$\begin{aligned} \dot{\sigma}_{PP} &= -i[\mathcal{P}H_S\mathcal{P}, \sigma_{PP}] \\ &+ \sum_{s\mu\kappa} [\mathcal{P}F_{\mu\kappa}^s\{c_{\kappa}^{\bar{s}}\}(\sigma_{PP} + \sigma_{QQ} + \sigma_{PQ} + \sigma_{QP})c_{\mu}^s\mathcal{P} \\ &\quad - \mathcal{P}c_{\mu}^s(\mathcal{P} + \mathcal{Q})F_{\mu\kappa}^s\{c_{\kappa}^{\bar{s}}\}(\sigma_{PP} + \sigma_{QP}) + \text{h.c.}], \\ \dot{\sigma}_{QQ} &= -i[\mathcal{Q}H_S\mathcal{Q}, \sigma_{QQ}] \\ &+ \sum_{s\mu\kappa} [\mathcal{Q}F_{\mu\kappa}^s\{c_{\kappa}^{\bar{s}}\}(\sigma_{PP} + \sigma_{QQ} + \sigma_{PQ} + \sigma_{QP})c_{\mu}^s\mathcal{Q} \\ &\quad - \mathcal{Q}c_{\mu}^s(\mathcal{P} + \mathcal{Q})F_{\mu\kappa}^s\{c_{\kappa}^{\bar{s}}\}(\sigma_{QQ} + \sigma_{PQ}) + \text{h.c.}], \\ \dot{\sigma}_{PQ} &= -i(\mathcal{P}H_S\mathcal{P}\sigma_{PQ} - \sigma_{PQ}\mathcal{Q}H_S\mathcal{Q}) \\ &+ \sum_{s\mu\kappa} [\mathcal{P}F_{\mu\kappa}^s\{c_{\kappa}^{\bar{s}}\}(\sigma_{PP} + \sigma_{QQ} + \sigma_{PQ} + \sigma_{QP})c_{\mu}^s\mathcal{Q} \\ &\quad - \mathcal{P}c_{\mu}^s(\mathcal{P} + \mathcal{Q})F_{\mu\kappa}^s\{c_{\kappa}^{\bar{s}}\}(\sigma_{QQ} + \sigma_{PQ}) + \text{h.c.}]. \end{aligned}$$

The high energy terms can be neglected since the energy cut will be chosen in such a way that all relevant eigenstates are below that energy so σ_{QQ} is approximately

zero. With the steady state condition $\dot{\sigma} = 0$ we examine from the second equation the dependence of the mixing terms $\sigma_{PQ} = \sigma_{QP}^\dagger$ from σ_{PP} :

$$\begin{aligned} \mathcal{R}(\sigma_{PQ}) &:= \sum_{s\mu\kappa} [\mathcal{Q}F_{\mu\kappa}^s\{c_{\kappa}^{\bar{s}}\}(\sigma_{PQ} + \sigma_{PQ}^\dagger)c_{\mu}^s\mathcal{Q} \\ &\quad - \mathcal{Q}c_{\mu}^s(\mathcal{P} + \mathcal{Q})F_{\mu\kappa}^s\{c_{\kappa}^{\bar{s}}\}\sigma_{PQ} + \text{h.c.}] \\ &= - \sum_{s\mu\kappa} [\mathcal{Q}F_{\mu\kappa}^s\{c_{\kappa}^{\bar{s}}\}\sigma_{PP}c_{\mu}^s\mathcal{Q} + \text{h.c.}] =: \mathcal{S}(\sigma_{PP}) \end{aligned}$$

The mixing terms σ_{PQ} represent coherences between eigenstates of a very high energy difference, thus they are rather small compared to the low energy part. Since in the term \mathcal{S} the dominant function $\mathcal{Q}F_{\mu\kappa}^s\{c_{\kappa}^{\bar{s}}\}\mathcal{P}$ depends on the energy differences of the high and low energy sectors it will be rather small for low applied voltages which justifies the approximation of σ_{PQ} to be negligible.

Using ERMEA the energy limit \mathcal{E} for the projection is successively increased till the convergence criteria (see the following section) are fulfilled. Thus we extend the representation basis of the superoperator by adding more and more higher energy states till convergence is reached.

D. Convergence parameters

For better illustration and to match the assumptions of the later discussed calculations we assume that the generator K is linear and does not depend on time.

To qualify the convergence of the linear generator K in the sense that the chosen energy cut \mathcal{E} is appropriate, the following features are checked:

a. Preservation of trace: The linear form of the superoperator K will be a matrix, acting on the vectorized reduced density operator $\sigma \rightarrow (\sigma_j)_{j \in I}$, where we use the index set I and later $I_d \subset I$ referencing to all elements [28] respectively to all diagonal elements of the reduced density operator. Since the dynamical map \mathcal{U} shall preserve the trace for all possible reduced density matrices, the time derivative of the trace shall be zero which leads to:

$$\begin{aligned} 0 &= \frac{d}{dt} \text{Tr}\{\sigma(t)\} = \text{Tr}\{K\sigma(t)\} = \sum_{i \in I_d} \sum_{j \in I} K_{ij} \sigma_j(t) \\ &= \sum_{j \in I} \sigma_j \underbrace{\left(\sum_{i \in I_d} K_{ij} \right)}_{\stackrel{!}{=} 0}. \end{aligned} \quad (10)$$

This motivates the definition of the **trace number**

$$\nu_t = \frac{1}{|I| \cdot |I_d|} \sum_{j \in I} \left| \sum_{i \in I_d} K_{ij} \right|, \quad (11)$$

which should be close to zero in order to indicate a constant trace one and the convergence of the approximated superoperator.

b. Preservation of hermiticity: Since a dynamical map inherits the property of preserving hermiticity from its generator K , we check the capability of the generator to fulfill Con. 2:

$$\begin{aligned}\dot{\sigma}_{ij} &\stackrel{!}{=} \dot{\sigma}_{ji}^*, \\ \sum_{lm \in I \otimes I} K_{ij,lm} \sigma_{lm} &\stackrel{!}{=} \left(\sum_{ml} K_{ji,ml} \sigma_{ml} \right)^* \\ &= \sum_{lm} K_{ji,ml}^* \sigma_{lm}.\end{aligned}$$

Since this has to be valid for all possible Hermitian density operators σ the following relation has to hold:

$$K_{ij,lm} \stackrel{!}{=} K_{ji,ml}^*. \quad (12)$$

A general theory about hermiticity and positivity preserving operators $T : \mathbb{C}^n \otimes \mathbb{C}^n \rightarrow \mathbb{C}^m \otimes \mathbb{C}^m$ can be derived using the Choi theorem [29, 30] based on the Choi matrix which is defined via

$$C(T) := \sum_{i,j \in I_n} E_{ij} \otimes T(E_{ij}) \in \mathbb{C}^{nm \times nm},$$

where $E_{ij} = |i\rangle\langle j|$ are unit basis vectors of the space $\mathbb{C}^n \otimes \mathbb{C}^n$. The theorem of Choi states that if the Choi matrix $C(T)$ is positive the operator T preserves positivity. As we show in App. B, the same holds true for hermiticity: the generator K preserves hermiticity if $C(K)$ is Hermitian.

We define the **hermiticity number** ν_h as the Frobenius norm of the anti-Hermitian part of $C(K)$:

$$\nu_h = \sqrt{\sum_{ijlm \in I} |A_{ij,lm}|^2}, \quad A = \frac{C(K) - C(K)^\dagger}{2}. \quad (13)$$

c. Preservation of positivity The required positivity of the time evolution is equivalent to the positivity of the exponential term $\exp(K)$: $\sigma(t) = e^{K(t-t_0)} \sigma(t_0) = \sum_{n \geq 0} \frac{1}{n!} (t-t_0)^n K^n \sigma(t_0)$. In order to qualify the positivity of this exponential term one could use Choi's theorem as described in the last paragraph and check whether the whole spectrum of the Choi matrix $\tilde{C}(\exp(K))$ is positive. Alternatively one can analyze the spectrum of K directly. As shown in [12, Th. 4.4] or [18] it is sufficient for positivity to show that the time evolution is a contraction

$$\|\exp(Kt)\| \leq 1,$$

given it preserves the trace. This condition is fulfilled if and only if all eigenvalues of K have a non-positive real part and its numerical verification can be combined with the search for the steady state (eigenvector of K to eigenvalue zero).

To qualify positivity we define the **positivity number** ν_p as the real part of the eigenvalue with largest real part

$$\nu_p := \max_{\lambda \in \sigma(K)} \text{Re}(\lambda), \quad (14)$$

which should be zero and identifies the unique steady state if the norm of this eigenvalue is also zero and no other eigenvalue with pure imaginary part exists.

III. SYMMETRIZED BORN-MARKOV MASTER EQUATION APPROACH

This section is dedicated to the ab-initio derivation of an effective Lindblad type master equation and to the encountered problems and possible extensions.

A straightforward microscopic derivation of the quantum master equation with the Born-Markov approximation which is exact in the weak-coupling limit, does not necessarily lead to a completely positive map. One can apply the so-called secular approximation which states that the density matrix is block diagonal in the system eigenstates corresponding to different eigenenergies which implies that any coherences between different energies are neglected. Though this leads to a master equation in Lindblad form which preserves positivity, it is fatal for the description of quasi-degenerate states which arise naturally in any realistic molecule. To account for this situation one could simply introduce a quasi-secular approximation [11, App. A] allowing coherences for quasi-degenerate states but with this approach (BMME type B) positivity and a Lindblad form cannot be guaranteed. As pointed out in [12, Ch.6.2.6] several workarounds have been proposed to avoid the secular approximation but still provide positivity, such as the non-Markovian dynamical coarse-graining for time evolution [31] or a time averaging approach [32].

In contrast to these methods we want to improve on the quasi-secular approximation allowing those energy states whose eigenenergies are close to each other ($|E_1 - E_2| < \Delta E$) to interact and therefore introduce a **symmetrized master equation**. We show that this BMME type C is of Lindblad form, allows for systematic analysis of positivity and features better convergence in terms of the trace preserving property (see Sec. IV).

The standard microscopic derivation (see App. A) leads to the following integro-differential equation:

$$\begin{aligned}\dot{\sigma}(t) &= \text{Tr}_B\{\mathcal{L}_0 \rho(t)\} + \mathcal{K}, \\ \mathcal{K} &:= \int_0^\infty \text{Tr}_B\{\mathcal{L}_I e^{\mathcal{L}_0 \tau} \mathcal{L}_I \rho(t-\tau)\} d\tau.\end{aligned} \quad (15)$$

The next step requires to perform the Markov approximation. Simply substituting $\rho(t-\tau)$ by $\rho(t)$ would lead to the term $e^{-iH_0 \tau} \mathcal{L}_I \rho(t) e^{iH_0 \tau}$. Using the Born approximation ($\rho(t) = \sigma(t) \otimes \rho_B$) and the secular approximation would guarantee that the decoupled Hamiltonian H_0 and ρ commute thus having detached the density operator from the integral. In our non-secular approach this is not possible, thus a more careful derivation has to be carried out. Simply setting $t-\tau$ to t is anyway a rather rough Markov approximation, a better approach is realized by approximating the time dependence of ρ on τ by

a time evolution with respect to the decoupled Hamiltonian H_0 : $\rho(t - \tau) \approx e^{-\mathcal{L}_0 \tau} \rho(t)$. The approximation is to replace the full Hamiltonian H by H_0 . In this manner we correct for the time shift by a unitary time evolution induced by the isolated system and bath. There are two ways of applying this approximation in Eq. (15):

1. Propagate before the interaction with the environment by substituting

$$\rho(t - \tau) \approx e^{-\mathcal{L}_0 \tau} \rho(t).$$

2. Propagate after the interaction with the environment by substituting

$$\mathcal{L}_I e^{\mathcal{L}_0 \tau} \mathcal{L}_I \rho(t - \tau) \approx e^{-\mathcal{L}_0 \tau} \mathcal{L}_I e^{\mathcal{L}_0 \tau} \mathcal{L}_I \rho(t).$$

The first approach leads to the BMME [see Eq. (6) and App. D], where the effective time evolution acts on the second coupling Liouville operator \mathcal{L}_I resulting in:

$$\begin{aligned} \mathcal{K}_1 &:= \int_0^\infty \text{Tr}_B \{ \mathcal{L}_I e^{H_0 \tau} \mathcal{L}_I e^{iH_0 \tau} \rho(t) e^{-iH_0 \tau} e^{iH_0 \tau} \} d\tau \\ &= \text{Tr}_B \{ \int_0^\infty \mathcal{L}_I e^{-iH_0 \tau} \mathcal{L}_I e^{iH_0 \tau} d\tau \rho(t) \}. \end{aligned} \quad (16)$$

One can also arrive at this equation by using the projection technique [12, Sec 6.2].

The second approach leads to a similar equation except with the difference that the time evolution acts on the first coupling Liouville operator \mathcal{L}_I :

$$\begin{aligned} \mathcal{K}_2 &:= \int_0^\infty \text{Tr}_B \{ e^{iH_0 \tau} \mathcal{L}_I e^{-iH_0 \tau} \mathcal{L}_I \rho(t) e^{iH_0 \tau} e^{-iH_0 \tau} \} d\tau \\ &= \text{Tr}_B \{ \int_0^\infty e^{iH_0 \tau} \mathcal{L}_I e^{-iH_0 \tau} \mathcal{L}_I dt' \rho(t) \}. \end{aligned} \quad (17)$$

Both approaches are also derived and discussed in the paper of Spohn and Dümcke where they are referred to as K_1 and K_2 [33].

The idea of the symmetrized Markov master equation is averaging both types of Markov approximations yielding

$$\dot{\sigma}(t) = -i \text{Tr}_B \{ [H_0, \rho(t)] \} + \frac{1}{2} (\mathcal{K}_1 + \mathcal{K}_2). \quad (18)$$

We show, that this BMME can be cast into Lindblad form without applying the secular approximation. Similar as done for the transformation of the secular BMME to Lindblad form (App. A 2) we apply the Born approximation and separate bath dependent terms from the system dependent terms to arrive at the following equation:

SYMMETRIC BORN-MARKOV MASTER EQUATION, TYPE C
$\begin{aligned} \dot{\sigma}(t) &= -i[H_S, \sigma(t)] \\ &\quad - \frac{1}{2} \sum_{s\mu\kappa} [c_\mu^s, F_{\mu\kappa}^s(\mathcal{L}_S) \{c_\kappa^{\bar{s}}\} \sigma(t)] + \text{h.c.} \\ &\quad - \frac{1}{2} \sum_{s\mu\kappa} [F_{\mu\kappa}^s(-\mathcal{L}_S) \{c_\mu^s\}, c_\kappa^{\bar{s}} \sigma(t)] + \text{h.c.}, \end{aligned} \quad (19)$

with the dissipators as defined in Eq. (7) [compare with Eq. (6)].

Decomposing the dissipators in Eq. (19) in Hermitian and anti-Hermitian part (see App. A 3 or [12, Ch.6.2.3]) leads to the form:

$$\begin{aligned} \dot{\sigma}(t) &= -i[H_S + H_{LS}, \sigma(t)] \\ &\quad + \frac{1}{2} \sum_{s\mu\kappa} \left(\gamma_{\mu\kappa}^s(-i\mathcal{L}_S) \{c_\kappa^{\bar{s}}\} \sigma(t) c_\mu^s \right. \\ &\quad \left. + c_\kappa^{\bar{s}} \sigma(t) \gamma_{\mu\kappa}^s(i\mathcal{L}_S) \{c_\mu^s\} \right. \\ &\quad \left. - \frac{1}{2} \{c_\mu^s \gamma_{\mu\kappa}^s(-i\mathcal{L}_S) \{c_\kappa^{\bar{s}}\}, \sigma(t)\} \right. \\ &\quad \left. - \frac{1}{2} \{ \gamma_{\mu\kappa}^s(i\mathcal{L}_S) \{c_\mu^s\} c_\kappa^{\bar{s}}, \sigma(t) \} \right), \end{aligned} \quad (20)$$

with the Lamb shift Hamiltonian

$$\begin{aligned} H_{LS} &:= -i \frac{1}{4} \sum_{s\mu\kappa} c_\mu^s \sigma_{\mu\kappa}^s(-i\mathcal{L}_S) \{c_\kappa^{\bar{s}}\} \\ &\quad - i \frac{1}{4} \sum_{s\mu\kappa} \sigma_{\mu\kappa}^s(i\mathcal{L}_S) \{c_\mu^s\} c_\kappa^{\bar{s}}. \end{aligned}$$

The Hermitian part of the dissipators becomes

$$\gamma_{\mu\kappa}^s(\omega) = \sum_{\alpha pl} V_{\alpha p \mu}^s i \underbrace{\left(G_{\alpha, \pi(s)(pl)}^R(s\omega) - G_{\alpha, \pi(s)(pl)}^A(s\omega) \right)}_{=: O_{\alpha, pl}^s(\omega)} \cdot f^{\bar{s}}(s\omega | \beta_\alpha, \mu_\alpha) V_{\alpha l \kappa}^{\bar{s}}. \quad (21)$$

The term $O_{\alpha,pl}^s(\omega)$ describes up to a factor of π the density of occupied states at energy ω in orbital pl of bath

α (density of states times Fermi distribution function). The expression for the anti-Hermitian term becomes

$$\sigma_{\mu\kappa}^s(\omega) = -\frac{1}{\pi} \sum_{\alpha pl} V_{\alpha p\mu}^s \mathcal{P} \int_{-\infty}^{\infty} \frac{(G_{\alpha,\pi(s)(pl)}^R(\omega') - G_{\alpha,\pi(s)(pl)}^A(\omega')) f_{\bar{s}}(\omega'|\beta_{\alpha}, \mu_{\alpha})}{\omega - s\omega'} d\omega' V_{\alpha l\kappa}^{\bar{s}}, \quad (22)$$

with the principle value integral \mathcal{P} , see App. A 3.

In the secular limit there holds Eq. (D2), thus we can identify BMME type C [Eq. (20)] with type A [Eq. (D4)].

In order to bring this master equation in Lindblad form and to examine positivity we use the system eigenvectors $|a\rangle, |b\rangle$ to define traceless operators $A_i = |a\rangle\langle b|$ (compare with App. D).

SYMMETRIC BORN-MARKOV MASTER EQUATION
IN LINDBLAD FORM USING THE SYSTEM
EIGENBASIS

$$\begin{aligned} \dot{\sigma}(t) = & -i[H_S + H_{LS}, \sigma(t)] \\ & + \sum_{abcd} \Gamma_{ab|cd} \left(|a\rangle\langle b| \sigma(t) |d\rangle\langle c| \right. \\ & \left. - \frac{1}{2} \{ |d\rangle\langle c| |a\rangle\langle b|, \sigma(t) \} \right), \end{aligned} \quad (23)$$

with the Gamma matrix

$$\Gamma_{ab|cd} = \sum_{\mu\kappa} \langle a|c_{\kappa}^{\bar{s}}|b\rangle \frac{\gamma_{\mu\kappa}^s(E_{ba}) + \gamma_{\mu\kappa}^s(E_{dc})}{2} \langle d|c_{\mu}^s|c\rangle \quad (24)$$

and energy differences $E_{ba} = E_b - E_a$. The value of $s = s(a, b)$ is given by the choice of the eigenvalues $|a\rangle$ and $|b\rangle$ and their corresponding particle numbers N_a and N_b with $s = N_b - N_a = \pm 1$, otherwise zero. Inserting Eq. (21) leads to

$$\begin{aligned} \Gamma_{ab|cd} = & \sum_{\alpha pl} \langle a| \sum_{\kappa} c_{\kappa}^{\bar{s}} V_{\alpha\kappa l}^s |b\rangle \frac{O_{\alpha,lp}^s(E_{ba}) + O_{\alpha,lp}^s(E_{dc})}{2} \\ & \cdot \langle d| \sum_{\mu} V_{\alpha p\mu}^{\bar{s}} c_{\mu}^s |c\rangle. \end{aligned} \quad (25)$$

The form of the matrix element $\Gamma_{ab|cd}$ (Eq. 25) resembles the structure $\Gamma_{ij} = v_i \cdot (w_i + w_j) \cdot v_j^*$ with vectors v and w . The positivity of Γ is determined by the eigenvalues

of the matrix W , $W_{ij} = (w_i + w_j)$ and are given by

$$\lambda_{1,2} = \sum_{i=1}^n \text{Re}(w_i) \pm \sqrt{n \sum_{i=1}^n |w_i|^2 - \left(\sum_{i=1}^n \text{Im}(w_i) \right)^2}, \quad (26)$$

whereas all other eigenvalues are zero. This way positivity cannot be guaranteed but still completely positive maps are possible depending on the properties of the baths. In the secular approximation the vector w is constant leading to one positive non-zero eigenvalue, thus having a guaranteed completely positive map.

IV. NUMERICAL BENCHMARK OF DESTRUCTIVE QUANTUM INTERFERENCE IN A 6-SITE MODEL

For testing ERMEA and the BMME type C we choose a fermionic six site model with quasi-degenerate eigenstates which features a destructive quantum interference (DQI) effect and which computationally is quite involved when building the full superoperator K .

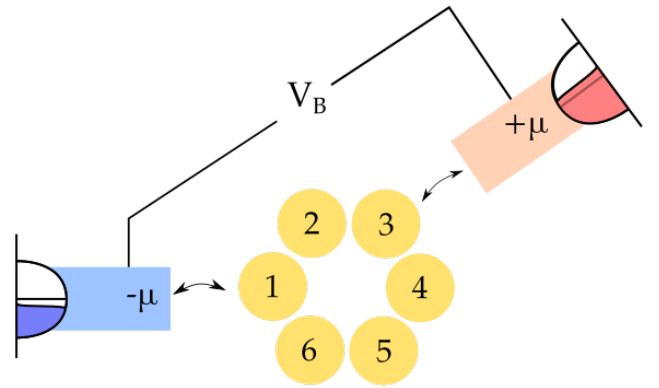


FIG. 2. Sketch of the fermionic six site system coupled to two leads in the meta configuration.

The system Hamiltonian is related to a D6h symmetric benzene molecule [11, 34] and is given in energy units of

electronvolts by

$$H_S = \sum_{\sigma, ij} T_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_{ij\sigma\sigma'} \frac{U_{ij}}{2} \left(n_{i\sigma} n_{j\sigma'} - \frac{n_{i\sigma} + n_{j\sigma'}}{2} \right),$$

$$T = \begin{pmatrix} -3.8 & -2 & -0.3 & -0.3 & -2 \\ -2 & -3.8 & -2 & -0.3 & -0.3 \\ -0.3 & -2 & -3.8 & -2 & -0.3 \\ & -0.3 & -2 & -3.8 & -2 & -0.3 \\ -0.3 & & -0.3 & -2 & -3.8 & -2 \\ -2 & -0.3 & & -0.3 & -2 & -3.8 \end{pmatrix}, \quad (27)$$

$$U = \begin{pmatrix} 8 & 5 & 3 & 2 & 3 & 5 \\ 5 & 8 & 5 & 3 & 2 & 3 \\ 3 & 5 & 8 & 5 & 3 & 2 \\ 2 & 3 & 5 & 8 & 5 & 3 \\ 3 & 2 & 3 & 5 & 8 & 5 \\ 5 & 3 & 2 & 3 & 5 & \mathbf{8.1} \end{pmatrix}.$$

The small deviation in the Coulomb repulsion on site six breaks the symmetry and all degeneracies of eigenstates in the same particle and spin sector vansish. Still some quasi-degenerate eigenstates with an energy gap $\Delta E < 0.1$ eV remain. The spectrum of this fermionic six site-system is depicted in Fig 3. The first excited states (circle) in the seven particle sector are such quasi-degenerate eigenstates.

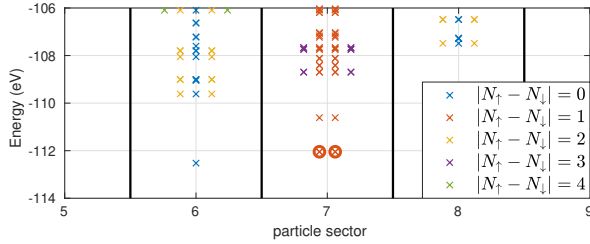


FIG. 3. Low energy spectrum of the six site system separated by particle and spin number. The spectrum ranges from -113 to 0 eV. The quasi-degenerate eigenstates in particle sector seven are marked by circles.

Attached to this six site model are two leads modeled by semi-infinite tight binding chains with an internal hopping of $t_B = 6$ eV (bandwidth = 24 eV) and zero on-site energies at temperature $\beta = 20$. The coupling to the central system [Eq. (5)] is given by $V_{L,1} = V_{R,3} = 0.1$ eV. The left resp. right lead couples to site one resp. site three, this contact scheme is called meta configuration (see also Fig. 2) which gives rise to DQI [35].

The non-equilibrium situation is realized by applying a bias voltage V_B on the leads by shifting the chemical potential $\mu_L = -\frac{V_B}{2}, \mu_R = \frac{V_B}{2}$ in the Fermi function.

A. Structure of the master equation

The system under consideration preserves the particle number and the spin. Thus the system Hamiltonian H_S

is block-diagonal in these quantities which also holds for bath Hamiltonian H_B . Since the coupling [see Eq. (5)] preserves total particle number and spin of system and bath, the reduced density matrix and its defining master equation will show the same block-diagonal structure. Applying the secular approximation restricts the reduced density matrix to be diagonal in its eigenenergies (all degeneracies lifted). The following table (Tab. II) compares the number of relevant elements of the density operator obtained from different assumptions on the block diagonal structure according to eigenenergies (the secular approximation, a quasi-secular approximation or no secular approximation). Spin and particle conservation are

TABLE II. Effect of block-diagonal-energy assumption on the dimension of the superoperator K . The size of the superoperator when using ERMEA depends on the applied bias voltage V_B .

Approximation in energy space	Dimension of superoperator
Secular approximation	4096
No secular approximation	853776
Quasi-secular approximation $\Delta E = 0.1$ eV	17050
ERMEA, $V_B = 5$ V, quasi-sec. approx.	4408

exploited in all three variants. If one neglects all interactions between different eigenenergies – especially the interactions between quasi-degenerate eigenenergies – then the destructive quantum interference is not obtained anymore as depicted in Fig. 8. Taking into account all interactions between different energy states (no secular approximation) would produce a rather large superoperator matrix K which would make the search for the steady state computationally very expensive. To take those interactions which are relevant into account and discard those which are not, it is convenient to pursue an intermediate approach of a **quasi-secular approximation** which considers interactions between eigenenergies with an energy difference lower than a specified value ΔE . By using ERMEA the size of the superoperator can further be shrunk as visualized in Fig. 5.

B. Convergence using ERMEA

We tested ERMEA by calculating the steady state density matrix and the related current using all three master equations (Tab. I).

The superoperator $K(\mathcal{E})$ is build within ERMEA by successively increasing the energy cut \mathcal{E} that defines up to which energy eigenstates are included in the computation of the superoperator. A shift in the energy cut can be performed by just including the next eigenstates with the subsequent eigenenergies in the construction of the superoperator. For each shift of the energy cut \mathcal{E} all quality factors introduced in Sec. IID are calculated to monitor the convergence of the superoperator $K(\mathcal{E})$.

With no applied voltage only the lowest eigenstates will contribute to the steady state and an effective superoperator preserving hermiticity, trace and positivity is easily calculated. Fig. 4 shows the convergence of the superoperator K via the quality factors for increasing energy cuts \mathcal{E} using master equation type B and C at a bias voltage of $V_B = 3.6$ V. It comes out clearly that the positivity number ν_p converges well and identically for both types. The hermiticity number ν_h is for both methods negligibly small [36] since the form of the master equation guarantees hermiticity independently from the chosen energy cut.

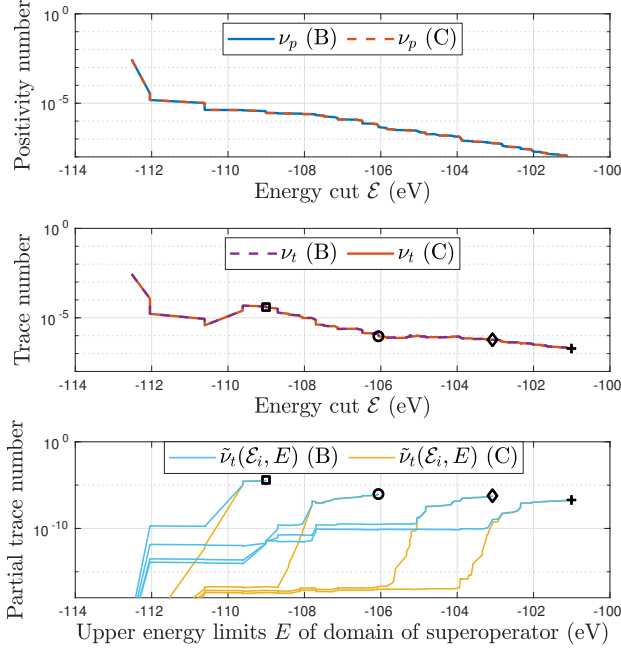


FIG. 4. Convergence trend of approximated superoperator $K(\mathcal{E})$ for an applied voltage of $V_B = 3.6$ V, using master equation type B [Eq. (6)] and type C [Eq. (23)] as a function of the energy cut \mathcal{E} . The upper panel shows the convergence of the positivity number ν_p which are the same for both methods. The middle panel depicts the trace number $\nu_t(\mathcal{E}_i)$ for both methods which are also the same. The lower panel compares the partial trace number $\tilde{\nu}_t(\mathcal{E}_i, E)$ for both methods for fixed energy cuts $\mathcal{E}_i = -109$ eV (square), -106 eV (circle), -103 eV (diamond) and -101 eV (plus) as a function of the domain restriction E . BMME type C shows a better trace preserving behavior than type B.

In order to examine the preservation of trace we introduce the partial trace number $\tilde{\nu}_t$:

$$\tilde{\nu}_t(\mathcal{E}, E) := \frac{1}{|I(E)| \cdot |I_d(E)|} \sum_{j \in I(E)} \left| \sum_{i \in I_d(E)} K_{ij}(\mathcal{E}) \right|, \quad (28)$$

which characterizes the trace preserving property of an already calculated superoperator $K(\mathcal{E})$ acting only on

density matrices with non-zero entries for eigenstates with an energy lower than the energy E . This number indicates how well the trace is preserved for the low energy domains on which the superoperator acts.

Four of these partial trace numbers are depicted in Fig. 4 and show that the trace preservation becomes worse for the higher energy terms a superoperator is acting on. The action of the approximated superoperator on high energy parts of a density matrix does not fulfill the trace preserving property. This is a clear artifact of the approximation since shifting the energy cut \mathcal{E} to higher energies repairs this failure for fixed eigenenergies E .

Therefore we introduced the following convergence criterion: We require that there is an energy $E < \mathcal{E}$ for which the partial trace number $\tilde{\nu}_t(\mathcal{E}, E)$ is converged (below a preset tolerance δ) and which acts as upper bound for the energies of non-negligible [37] entries in the calculated steady state density matrix. This criterion reflects the demand of having a trace preserving superoperator at least for the domain which is relevant for the calculated steady state. For a time evolution one should set the threshold in such a way that the superoperator works well for a domain containing all accessible energies.

For the partial trace number $\tilde{\nu}_t$, type C shows a better convergence than type B.

Fig. 5 shows the computational effort to reach convergence using type C and the final convergence parameters as a function of applied bias voltage V_B for the tolerances $\delta = 10^{-6}$ and $\delta = 10^{-7}$. In addition $\Delta\sigma$ depicts the Frobenius norm of the difference of the steady state density matrices obtained with the tolerances $\delta = 10^{-6}$ and $\delta = 10^{-7}$.

After having calculated a converged superoperator K we calculate the steady state of the system which is given by the eigenvector of K to the eigenvalue zero. To illustrate the spectral properties we show the spectrum of the converged superoperator for a bias voltage of $V_B = 3.6$ V in Fig. 6. One can clearly see that all but one of the eigenvalues have a negative real part, which reflects the dissipative properties of the derived master equation.

Fig. 7 shows the distribution of the steady state density matrix entries and the used energy cut \mathcal{E} (dashed line) to fulfill the convergence criteria as a function of applied bias voltage V_B . The tolerance δ was set to 10^{-7} . The first excited quasi-degenerate eigenstates (dark green) are the dominant states in the steady state situation over a wide voltage range.

Finally we present the current in Fig. 8 using the current formula derived in App. C to emphasize the importance of taking quasi-degenerate eigenstates into account. These states build up strong correlations visible in the large off-diagonal entries of the steady state density matrix. The current was calculated depending on the applied bias voltage V_B for the three discussed master equations type A, B and C. The secular approximation clearly fails to display the destructive quantum interference in this setup.

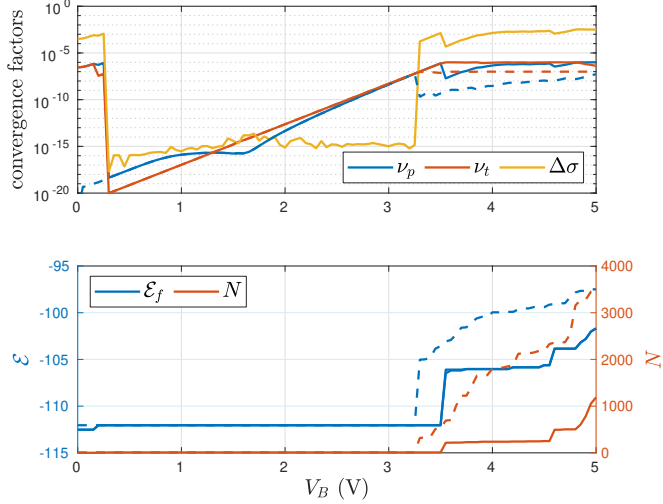


FIG. 5. Convergence factors, final energy cut \mathcal{E}_f and size N of converged superoperator and error of steady state density matrix $\Delta\sigma$ as a function of applied bias voltage V_B for used tolerances of $\delta = 10^{-6}$ (solid lines) and $\delta = 10^{-7}$ (dashed lines). Upper panel: Absolute value of positivity number ν_p and partial trace number ν_t of the converged superoperator as well as total error of resulting density operator $\Delta\sigma$ with a used tolerance of $\delta = 10^{-6}$ compared to the density operator obtained with a tolerance of $\delta = 10^{-7}$. Lower panel, left axis: Final energy cut \mathcal{E}_f of converged superoperator; right axis: Final dimension N of the converged superoperator for a tolerance of $\delta = 10^{-6}$ (solid line) and $\delta = 10^{-7}$ (dashed line).

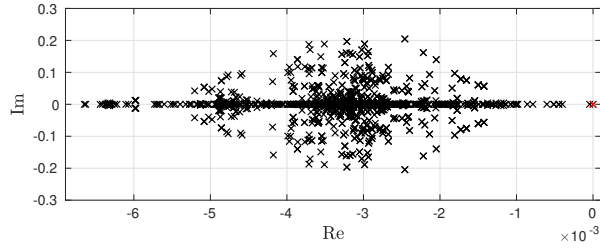


FIG. 6. Spectrum of the eigenvalues of the superoperator K for an applied bias voltage of $V_B = 3.6$ V. The steady state eigenvector to eigenvalue zero is marked in red.

V. CONCLUSION

We show that the energy resolved master equation approach improves the computability of steady state density matrices of open quantum systems. It may contribute to adopt more advanced master equation techniques to larger systems. Especially the quality factors provide a useful tool on the decision of convergence of approximatively calculated superoperators. We derived a new Lindblad type master equation for the quasi-degenerate states (type C) and compared it to conventional Born–Markov master equation approaches. Type C shows strong improvements in the stability of the re-

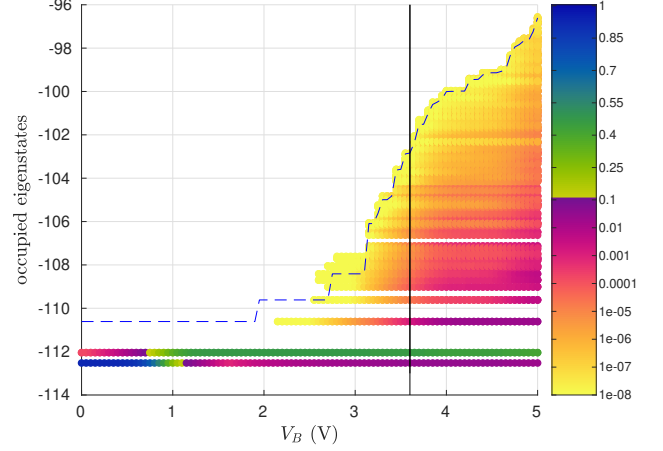


FIG. 7. Distribution of entries of the steady state density matrix according to their eigenenergies as a function of applied bias voltage V_B . The dashed line corresponds to the energy E where the partial trace number criterion was fulfilled for a used tolerance of $\delta = 10^{-7}$. The black solid line marks the voltage V_B for which the convergence trend of the approximated superoperator is discussed in Fig. 4.

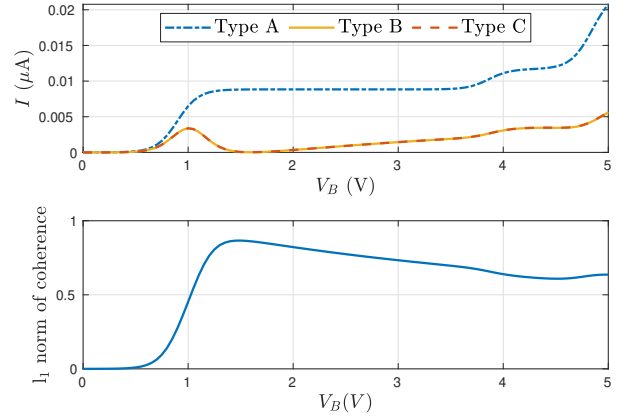


FIG. 8. Upper panel: Current calculated for the six-site system with methods A, B and C for different applied bias voltages V_B . The occurring interference effects are not reproduced with the type A method, because it neglects the quasi-degenerate states and thus cannot reproduce the rising coherences between those states. Lower panel: Rising coherences as l_1 norm of off-diagonal matrix elements of the resulting density matrix as a function of applied bias voltage V_B .

tained solutions as compared to the commonly used type B.

ACKNOWLEDGEMENT

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Appendix A: Microscopic derivation

1. Derivation of the integro-differential equation

We start with the Schrödinger equation for the full system (\hbar is set to one):

$$\dot{\rho}(t) = -i[H, \rho(t)].$$

We switch to the interaction picture, which will be denoted by bold symbols, $\boldsymbol{\rho}(t) = e^{iH_0(t-t_0)}\rho(t)e^{-iH_0(t-t_0)}$. The Schrödinger equation in the interaction picture reads:

$$\dot{\boldsymbol{\rho}}(t) = -i[\mathbf{H}_I(t), \boldsymbol{\rho}(t)].$$

We integrate this equation from a starting point t_0 where system and bath are decoupled $\rho(t_0) = \sigma(t_0) \otimes \rho_b(t_0)$

$$\boldsymbol{\rho}(t) = \boldsymbol{\rho}(t_0) - i \int_{t_0}^t [\mathbf{H}_I(t'), \boldsymbol{\rho}(t')] dt'.$$

Reinsertion into the Schrödinger equation generates a integro-differential equation:

$$\dot{\boldsymbol{\rho}}(t) = -i[\mathbf{H}_I(t), \boldsymbol{\rho}(t_0)] - \int_0^t [\mathbf{H}_I(t), [\mathbf{H}_I(t'), \boldsymbol{\rho}(t')]] dt'.$$

Going back to the Schrödinger picture by using

$$\begin{aligned} \frac{d}{dt}\boldsymbol{\rho}(t) &= e^{iH_0(t-t_0)} i[H_0, \rho(t)] e^{-iH_0(t-t_0)} \\ &+ e^{iH_0(t-t_0)} \left(\frac{d}{dt}\rho(t) \right) e^{-iH_0(t-t_0)}, \end{aligned}$$

and multiplying with $e^{-iH_0\underline{t}}$ from the left and $e^{iH_0\underline{t}}$ from the right using $\underline{t} = t - t_0$ leads to

$$\begin{aligned} \dot{\rho}(\underline{t}) &= -i[H_0, \rho(\underline{t})] \\ &- ie^{-iH_0\underline{t}}[e^{iH_0\underline{t}}H_Ie^{-iH_0\underline{t}}, \rho(t_0)]e^{iH_0\underline{t}} \\ &- \int_{t_0}^t \left[H_I, e^{-iH_0(t-t')} [H_I, \rho(t')] e^{iH_0(t-t')} \right] dt'. \end{aligned}$$

Since we are only interested in a dynamical map of the central system we trace out the bath and define the reduced density operator $\sigma(\underline{t}) := \text{Tr}_B\{\rho(\underline{t})\}$.

$$\begin{aligned} \dot{\sigma}(\underline{t}) &= \text{Tr}_B\{\dot{\rho}(\underline{t})\} \\ &= -i\text{Tr}_B\{[H_0, \rho(\underline{t})]\} - \underbrace{i\text{Tr}_B\{[H_I, \rho(t_0)]\}}_{=0} \\ &- \int_{t_0}^t \text{Tr}_B\left\{ \left[H_I, e^{-iH_0(t-t')} [H_I, \rho(t')] \right] \right. \\ &\quad \left. \cdot e^{iH_0(t-t')} \right\} dt'. \end{aligned}$$

The second term vanishes as the interaction Hamiltonian commutes with the decoupled state $\rho(t_0)$. The variable transformation ($\tau = t - t'$) with $dt' = -d\tau$, $\tau \in [t - t_0, 0]$ and the flipped limits induce

$$\begin{aligned} \dot{\sigma}(\underline{t}) &= -i\text{Tr}_B\{[H_0, \rho(\underline{t})]\} \\ &- \int_0^{t-t_0} d\tau \text{Tr}_B\{[H_I, e^{-iH_0\tau} [H_I, \rho(t-\tau)] e^{iH_0\tau}]\}. \end{aligned}$$

The next steps include sending t_0 to minus infinity as the interaction shall have been switched on adiabatically at that time. That way we end up with the still exact non-Markovian integro differential equation [see Eq. (15)] using Liouville operators.

2. Applying Born approximation, deriving Born-Markov master equation

After applying the Markov approximation to obtain \mathcal{K}_1 as discussed in III we perform the Born approximation in the integral (expansion term) which states that the density operator can be written as a tensor product at any time $\rho(t) \approx \rho_B \otimes \sigma(t)$. Inserting the commutators with H_I and separating bath and system components leads to

$$\begin{aligned} \mathcal{K}_1 &= - \int_0^\infty \text{Tr}_B\{[H_I, e^{-iH_0\tau} [H_I, \\ &\quad \rho_B e^{iH_S\tau} \sigma(t) e^{-iH_S\tau}] e^{iH_0\tau}\} d\tau \\ &= - \int_0^\infty \sum_{\mu\kappa s} [c_\mu^s, C_{\mu\kappa}^s(\tau) e^{-iH_S\tau} c_\kappa^s e^{iH_S\tau} \sigma(t)] + h.c. \end{aligned}$$

3. Decomposition of dissipators and expression in terms of equilibrium Green functions

In order to decompose the dissipators [see Eq. (7)] it is convenient to introduce the Hermitian and anti-Hermitian functions $(\gamma_{\mu\kappa}^s(\omega))^\dagger = \gamma_{\kappa\mu}^s(\omega)$ and $(\sigma_{\mu\kappa}^s(\omega))^\dagger = -\sigma_{\kappa\mu}^s(\omega)$ via

$$\gamma_{\mu\kappa}^s(\omega) := \int_{-\infty}^\infty C_{\mu\kappa}^s(\tau) e^{i\omega\tau} d\tau, \quad (\text{A1})$$

$$\sigma_{\mu\kappa}^s(\omega) := \int_{-\infty}^\infty C_{\mu\kappa}^s(\tau) \text{sign}(\tau) e^{i\omega\tau} d\tau, \quad (\text{A2})$$

$$F_{\mu\kappa}^s(i\omega) = \frac{\gamma_{\mu\kappa}^s(\omega) + \sigma_{\mu\kappa}^s(\omega)}{2}.$$

The aim will be to express the influence of the baths in the equations above in terms of retarded and advanced Green functions G^R and G^A .

Starting from Eq. (8) we identify the bath correlation functions $C_{\mu\kappa}^s(\tau)$ with the greater and lesser Green functions $G^+ = G^>$, $G^- = G^<$:

$$\langle d_{\kappa\alpha}^s(\tau) d_{l\alpha}^s \rangle = i s G_{\pi(s)(kl)}^s(s\tau),$$

using the permutation operator

$$\pi(-)(lp) = pl, \quad \pi(+)(lp) = lp.$$

The evaluation of this expression in the integral of Eq. (A1) reproduces the Fourier transform of the Green functions and leads to Eq. (21). The integration in Eq. (A2) can be interpreted as principle value integral:

$$\begin{aligned} & \int_{-\infty}^{\infty} g(\tau) \text{sign}(\tau) e^{i\omega\tau} d\tau \\ &= \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} g(\omega') \int_{-\infty}^{\infty} \text{sign}(t) e^{i(\omega-\omega')\tau - \varepsilon|\tau|} d\tau \\ &= \frac{i}{\pi} \int_{-\infty}^{\infty} g(\omega') \frac{\overbrace{\omega - \omega'}^{x:=}}{(\omega - \omega')^2 + \varepsilon^2} d\omega' \\ &= \frac{i}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{g(\omega - x)}{x} dx, \end{aligned}$$

leading to Eq. (22).

Since the bath is in equilibrium, greater and lesser Green functions can be expressed via

$$G_{ij}^s(\omega) = s(G_{ij}^R(\omega) - G_{ij}^A(\omega)) f^{\bar{s}}(\omega|\beta_\alpha, \mu_\alpha),$$

with the generalized Fermi function $f^-(\omega|\beta_\alpha, \mu_\alpha) = \frac{1}{e^{\beta_\alpha(\omega - \mu_\alpha)} + 1}$, $f^+ = 1 - f^-$, the bath temperature β_α and the chemical potential μ_α .

Appendix B: Choi theorem for the preservation of hermiticity

Calculating the Choi matrix in the present vectorized notation leads to

$$\begin{aligned} E_{12} \otimes K(E_{12}) &= \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \otimes K \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \\ &= \begin{pmatrix} 0 & 0 & K_{11,12} & K_{12,12} \\ 0 & 0 & K_{21,12} & K_{22,12} \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \end{aligned}$$

Comparing the original operator K and the Choi matrix $C(K)$ in this vectorized basis

$$\underbrace{(1,1)}_1, \underbrace{(2,1)}_2, \dots, \underbrace{(n,1)}_n, \underbrace{(1,2)}_{n+1}, \dots, (1,n), (2,n), \dots, \underbrace{(n,n)}_{n^2},$$

$$\begin{aligned} K &= \begin{pmatrix} K_{11,11} & K_{11,21} & K_{11,12} & K_{11,22} \\ K_{21,11} & K_{21,21} & K_{21,12} & K_{21,22} \\ K_{12,11} & K_{12,21} & K_{12,12} & K_{12,22} \\ K_{22,11} & K_{22,21} & K_{22,12} & K_{22,22} \end{pmatrix}, \\ C(K) &= \begin{pmatrix} K_{11,11} & K_{12,11} & K_{11,12} & K_{12,12} \\ K_{21,11} & K_{22,11} & K_{21,12} & K_{22,12} \\ K_{11,21} & K_{12,21} & K_{11,22} & K_{12,22} \\ K_{21,21} & K_{22,21} & K_{21,22} & K_{22,22} \end{pmatrix}, \end{aligned}$$

reveals an easy way to calculate $C(K)$ by swapping two indices in K :

$$C(K)_{ij,lm} = K_{il,jm}.$$

Using this relation we can express Eq. (12) via the Choi matrices C :

$$C(K)_{il,jm} \stackrel{!}{=} C(K)_{jm,il}^* \Rightarrow C(K) \stackrel{!}{=} C(K)^\dagger, \quad (\text{B1})$$

which proves the stated Choi criterion for K to preserve hermiticity.

Appendix C: Current formula for a Lindblad type master equation

Referring to the Lindblad equation [see Eq. (4)], the current is given by the time derivative of the total number of particles \hat{N}

$$\begin{aligned} I(t) &= \frac{e}{\hbar} \frac{d}{dt} \langle \hat{N}(t) \rangle = \frac{e}{\hbar} \frac{d}{dt} \text{Tr}\{\hat{N}\sigma(t)\} \\ &= -i \frac{e}{\hbar^2} \underbrace{\text{Tr}\{\hat{N}[H_S + H_{LS}, \sigma(t)]\}}_{\text{Tr}\{[\hat{N}, H_S + H_{LS}]\sigma(t)\}=0} \\ &\quad + \frac{e}{\hbar} \text{Tr}\left\{\frac{1}{2} \sum_{ij} \Gamma_{ij} \hat{N} [A_i, \sigma(t) A_j^\dagger] + h.c.\right\} \\ &= \frac{e}{\hbar} \sum_{ij} \text{ReTr}\{\Gamma_{ij} [\hat{N}, A_i] \sigma(t) A_j^\dagger\}. \end{aligned}$$

Using the eigenbasis operators and with the definition of $s(a, b)$ in Eq. (24) we gain for the current along lead α

$$\begin{aligned} I_\alpha(t) &= \frac{e}{\hbar} \sum_{ab,cd} \text{ReTr}\{\Gamma_{ab|cd}^\alpha \underbrace{[\hat{N}, |a\rangle\langle b|]}_{=N_a - N_b = -s} \sigma|d\rangle\langle c|\} \\ &= -\frac{e}{\hbar} \sum_{abd} s(a, b) \text{Re}\Gamma_{ab|ad}^\alpha \langle b|\sigma|d\rangle. \end{aligned} \quad (\text{C1})$$

Appendix D: Secular Born–Markov master equation and link to Lindblad form

Starting from BMME type B [see Eq. (6)] and after decomposing the dissipators F as illustrated in App. A 3 we gain for the dissipative part \mathcal{K}

$$\begin{aligned} \mathcal{K}_1 &= -\frac{1}{2} \sum_{s\mu\kappa} [c_\mu^s, \gamma_{\mu\kappa}^s (-i\mathcal{L}) \{c_\kappa^{\bar{s}}\} \sigma(t)] \\ &\quad + [c_\mu^s, \sigma_{\mu\kappa}^s (-i\mathcal{L}) \{c_\kappa^{\bar{s}}\} \sigma(t)] \\ &\quad + [\sigma(t) \gamma_{\mu\kappa}^s (i\mathcal{L}) \{c_\mu^s\}, c_\kappa^{\bar{s}}] \\ &\quad - [\sigma(t) \sigma_{\mu\kappa}^s (i\mathcal{L}) \{c_\mu^s\}, c_\kappa^{\bar{s}}]. \end{aligned}$$

Inserting full sets of eigenbasis vectors of the system Hamiltonian, having $H_S|a\rangle = E_a|a\rangle$, with the eigenvectors $|a\rangle$ and eigenenergies E_a , induces in the first term of

the first commutator

$$\sum_{abcde} |a\rangle \langle a| c_\mu^s |b\rangle \langle b| |d\rangle \langle d| \gamma_{\mu\kappa}^s (-\mathcal{L}) \{c_\kappa^{\bar{s}}\} |c\rangle \langle c| \sigma(t) |e\rangle \langle e|. \quad (\text{D1})$$

Applying the secular approximation implies the reduced density matrix to be block diagonal in its eigenenergies thus having $E_a = E_c = E_e$, since only contributions of \mathcal{K}_{ae} for the same energies are relevant for $\dot{\sigma}$. The set of eigenvectors $|d\rangle$ was inserted to motivate the later used traceless operators A_i in the Lindblad form. It holds $E_b = E_d$. Since functions of the Liouville superoperator are evaluated according to Eq. (9) we gain the following relation for the occurring pairs of creation and annihilation operators in the secular approximation:

$$c_\mu^s F_{\mu\kappa}^s (\mathcal{L}) \{c_\kappa^{\bar{s}}\} = F_{\mu\kappa}^s (-\mathcal{L}) \{c_\mu^s\} c_\kappa^{\bar{s}}, \quad (\text{D2})$$

because the occurring energy differences on both sides of a creation and annihilation operators will be equal except for one sign. Finally we can condense \mathcal{K} to

$$\mathcal{K}_1 = \sum_{s\mu\kappa} c_\kappa^{\bar{s}} \sigma(t) \gamma_{\mu\kappa}^s (i\mathcal{L}) \{c_\mu^s\} - \frac{1}{2} \{ \gamma_{\mu\kappa}^s (i\mathcal{L}) \{c_\mu^s\} c_\kappa^{\bar{s}}, \sigma(t) \} + [\sigma_\mu^s (i\mathcal{L}) \{c_\mu^s\} c_\kappa^{\bar{s}}, \sigma(t)], \quad (\text{D3})$$

where the Lamb-shift and the anti-commutator arising in the Lindblad form can already be identified. In the next steps we introduce an appropriate traceless operator basis needed in Lindblad form and derive the Γ matrices and prove positivity for the secular approximation.

1. Choice of the operator basis:

A practical choice for the traceless operators A_i used in the Lindblad equation [see Eq. (4)] can be constructed from the eigenbasis of the system S : $A_i = |a\rangle \langle b|$ such that $\langle a|b\rangle = 0$. Since the examined system Hamiltonians conserve spin and particle number, the eigenvectors belonging to different particle sectors M, N have per se no overlap $\langle a^{(N)} | b^{(M)} \rangle = 0$ for $M \neq N$.

a. Consequence of the perturbative approach: One clear consequence of the perturbative approach in the microscopic derivation of the BMME is that not the full range of possible traceless operators A_i in the Lindblad form is used. Due to the Born approximation in the expansion to second order only pairs of interaction Hamiltonians H_I and due to conservation of particle in the bath and in the system only pairs of annihilation and creation operators occur. This leads to mixtures of eigenstates which belong to neighboring particle and spin sectors. Traceless operators in the eigenbasis of the form $A_i = |a\rangle \langle b|$ always fulfill $\langle a|N|a\rangle - \langle b|N|b\rangle = \pm 1$.

2. Form of the Gamma matrices in the secular approximation:

Using the secular approximation, the Gamma matrices $\Gamma_{ij}, i = (a, b), j = (c, d)$ have non-zero entries only for those values where $E_a = E_c$ and $E_b = E_d$ hold. Referring to Eq. (D1) and Eq. (D3) we obtain the Lindblad equation [Eq. (4)] with

$$\begin{aligned} \Gamma_{ij} &= \sum_{\mu\kappa} \langle a | c_\kappa^{\bar{s}} | b \rangle \cdot \gamma_{\mu\kappa}^s \underbrace{(E_a - E_b)}_{=E_c - E_d} \cdot \langle d | c_\mu^s | c \rangle, \\ A_i &= |a\rangle \langle b|, \\ A_j &= |d\rangle \langle c|, \\ H_{LS} &= -i \sum_{s\mu\kappa} \sigma_{\mu\kappa}^s (i\mathcal{L}) \{c_\mu^s\} c_\kappa^{\bar{s}}. \end{aligned} \quad (\text{D4})$$

Note that s is determined by the choice of i since the state b is in the particle sector $N + s$ given that a is in sector N . For a nonzero entry in Γ index j has to follow this diction of particle sectors since to particle conservation.

3. Positivity in the secular approximation

It is shown (see also [10]) that using the secular approximation in the BMME the Gamma matrices are guaranteed to be positive semidefinite. Since we have non-diagonal entries only in the case of degenerate eigenstates, we assume to have degenerate eigenstates $|a\rangle$ and $|b\rangle$ with energies E_1 and eigenstates $|c\rangle$ and $|d\rangle$ with eigenenergies E_2 in a neighboring particle sector. Due to the secular approximation all energy differences in the argument of $\gamma_{\mu\kappa}^s (E_a - E_b)$ are the same. Via diagonalization $\gamma^s(\Delta E) = U D U^\dagger$, with $D = \text{diag}(d_1, \dots)$ we gain

$$\begin{aligned} \Gamma_{ij} &= \sum_k \underbrace{\langle a | \sum_{\kappa} c_\kappa^{\bar{s}} U_{\kappa k} | b \rangle}_{v_i^{(k)}} d_k \underbrace{\langle d | \sum_{\mu} U_{k\mu}^\dagger c_\mu^s | c \rangle}_{v_j^{(k)*}}, \\ \Gamma &= \sum_k d_k \vec{v}^{(k)} (\vec{v}^{(k)})^\dagger. \end{aligned}$$

Thus Γ is positive semidefinite iff γ^s is positive semidefinite ($d_k \geq 0, \forall k$).

a. Proof that $\gamma^s(\Delta E)$ is positive semidefinite in the microscopic derivation for a fixed energy difference From the microscopic derivation we got (see App. A 3)

$$\gamma_{\mu\kappa}^s(\omega) = i \sum_{\alpha\beta l} V_{\alpha\beta\mu}^s f^{\bar{s}}(\omega) (G^R(\omega) - G^A(\omega)) V_{\alpha l \kappa}^{\bar{s}},$$

with the (inverse) Fermi function $f, f^- = 1 - f$. Since the Green functions resemble the density of states $i(G_R - G_A) = \frac{1}{\pi} \text{DOS}(\omega) \geq 0$ and $0 \leq f^\pm(\omega) \leq 1$ we gain a positive value between the coupling vectors (matrices)

V. If the bath consists of more orbitals the expression $f^s(\omega)(G^R - G^A)$ is positive semidefinite. Multiplying the

adjoint coupling vectors V and V^\dagger on the DOS matrices conserves the positive semi-definiteness of the matrix γ^s (for all baths).

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