

Quantum thermodynamics and open-systems modeling

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ABSTRACT

A comprehensive approach to modeling open quantum systems consistent with thermodynamics is presented. The theory of open quantum systems is employed to define system bath partitions. The Markovian master equation defines an isothermal partition between the system and bath. Two methods to derive the quantum master equation are described: the weak coupling limit and the repeated collision model. The role of the eigenoperators of the free system dynamics is highlighted, in particular, for driven systems. The thermodynamical relations are pointed out. Models that lead to loss of coherence, i.e., dephasing are described. The implication of the laws of thermodynamics to simulating transport and spectroscopy is described. The indications for self-averaging in large quantum systems and thus its importance in modeling are described. Basic modeling by the surrogate Hamiltonian is described, as well as thermal boundary conditions using the repeated collision model and their use in the stochastic surrogate Hamiltonian. The problem of modeling with explicitly time dependent driving is analyzed. Finally, the use of the stochastic surrogate Hamiltonian for modeling ultrafast spectroscopy and quantum control is reviewed.

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I. INTRODUCTION

Any quantum system is influenced by its environment. As a result, dynamical modeling of molecular encounters has to incorporate open system strategies where the primary part of the system is treated explicitly and the rest, the bath implicitly. This approach is termed “reduced description” and is the subject of this overview.

Sound theoretical modeling ideally should be based on the controlled approximation based on the laws of nature. Open system dynamics is a quantum theory with the additional caveat that it should be consistent with thermodynamics. For example, in transport, does heat always flow from a hot to a cold reservoir?

A central issue in open quantum systems is defining the boundary between the system and its environment. We will follow ideas from thermodynamics and define ideal partitions, partitions that separate the system and bath but allow transport. The isothermal partition is a primary example allowing mutual heat flow but maintaining the definition of system and bath variables. Another

example is a chemical partition allowing the “in and out” flow of particles.

We will show how the theoretical framework of quantum thermodynamics is incorporated in dynamical simulations of open systems. A molecular context can illuminate these concepts. Molecular spectroscopy in solution is the theme of a chromophore absorbing radiation and sharing the excitation with the surrounding solvent where it is dissipated. The consequence is that we focus on externally driven open quantum systems.

In molecular physics, open quantum systems are prevalent. Molecular spectroscopy in the condensed phase,¹ in particular, ultrafast pump-probe²⁻⁷ and 2-D spectroscopy.^{8,9} Quantum biology is also a typical example.¹⁰⁻¹²

A. The von Neumann mathematical formalism of open systems

von Neumann was the first to realize that the wavefunction formulation of quantum mechanics is incomplete.¹³ The source of the discrepancy is due to quantum entanglement. Even if a combined

system is pure where its state is described by a wavefunction ψ_{SB} , due to entanglement, a subsystem state cannot be described by a wavefunction. By measuring only local system observables, one cannot distinguish between an entangled system and a statistical mixture. To solve this issue, von Neumann established the following fundamental structure of *quantum probability*:¹³

- (i) Quantum observables are represented by self-adjoint (Hermitian) operators (denoted by $\hat{\mathbf{A}}, \hat{\mathbf{B}}, \dots$) acting on the Hilbert space \mathcal{H} .
- (ii) Quantum events are the particular *yes-no* observables described by projectors ($\hat{\mathbf{P}} = \hat{\mathbf{P}}^2$).
- (iii) The state of the system is represented by density matrices, i.e., positive operators with trace one (denoted by $\hat{\rho}, \hat{\sigma}, \dots$).
- (iv) Probability of the event $\hat{\mathbf{P}}$ for the state $\hat{\rho}$ is given by

$$\mathcal{P} = \text{Tr}(\hat{\rho}\hat{\mathbf{P}}). \quad (1)$$

- (v) An averaged value of the observable $\hat{\mathbf{A}}$ at the state $\hat{\rho}$ is equal to

$$\langle \hat{\mathbf{A}} \rangle_{\rho} = \text{Tr}(\hat{\rho}\hat{\mathbf{A}}). \quad (2)$$

The dynamics of a closed quantum system is described by a unitary map \mathcal{U}_t ,

$$\hat{\rho}(t) = \mathcal{U}_t\hat{\rho}(0) \equiv \hat{\mathbf{U}}(t)\hat{\rho}(0)\hat{\mathbf{U}}^\dagger(t), \quad (3)$$

where $\hat{\mathbf{U}}$ is a unitary operator generated by the Hamiltonian operator $\hat{\mathbf{H}}(t)$,

$$\frac{d}{dt}\hat{\mathbf{U}}(t) = -\frac{i}{\hbar}\hat{\mathbf{H}}(t)\hat{\mathbf{U}}(t) \quad (4)$$

with $\hat{\mathbf{U}}(0) = \hat{\mathbf{1}}$. For time independent Hamiltonians, $\hat{\mathbf{U}}(t) = \exp\{-\frac{i}{\hbar}\hat{\mathbf{H}}t\}$. An equivalent differential form of the dynamics is described by the von Neumann evolution equation with the time-dependent Hamiltonian $\hat{\mathbf{H}}(t)$,

$$\frac{d}{dt}\hat{\rho}(t) = -\frac{i}{\hbar}[\hat{\mathbf{H}}(t), \hat{\rho}(t)]. \quad (5)$$

Quantum entropy was also introduced by von Neumann now known as the von Neumann entropy, defined by

$$\mathcal{S}_{vn}(\hat{\rho}) = -k_B \text{Tr}(\hat{\rho} \ln \hat{\rho}) = -k_B \sum_j \lambda_j \ln \lambda_j \geq 0, \quad (6)$$

where $\hat{\rho} = \sum_j \lambda_j |j\rangle\langle j|$ is a spectral decomposition of the density operator. The von Neumann entropy is an invariant of the state $\hat{\rho}$ and invariant to unitary dynamics [Eq. (5)]. In addition, it is the lower bound for all possible diagonal entropies $\mathcal{S}_A(\hat{\rho}) \geq \mathcal{S}_{vn}(\hat{\rho})$, where $\mathcal{S}_A = -k_B \sum_j p_j \ln p_j$ is the Shannon entropy defined by the probability distribution obtained by a complete measurement of the operator $\hat{\mathbf{A}}$.

The quantum counterpart of the canonical (Gibbs) ensemble, corresponding to the thermodynamic equilibrium state at the temperature T , for the system with the Hamiltonian $\hat{\mathbf{H}}$, is described by the density matrix of the form

$$\hat{\rho}_\beta = \frac{1}{Z} e^{-\beta\hat{\mathbf{H}}}, \quad \beta = \frac{1}{k_B T}, \quad Z = \text{Tr}\{e^{-\beta\hat{\mathbf{H}}}\}. \quad (7)$$

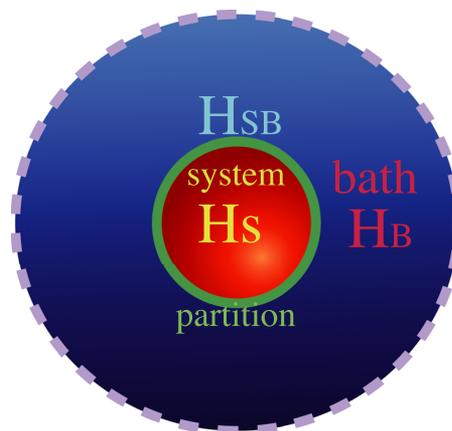


FIG. 1. System embedded in a bath. $\hat{\mathbf{H}} = \hat{\mathbf{H}}_S + \hat{\mathbf{H}}_B + \hat{\mathbf{H}}_{SB}$.

The Gibbs state maximizes entropy under the condition of a fixed mean energy (internal energy in thermodynamic language) $E = \text{Tr}(\hat{\rho}\hat{\mathbf{H}})$ or minimizes E for a fixed entropy \mathcal{S}_{vn} . In this case, $\mathcal{S}_{vn} = \mathcal{S}_H$.

We now consider a bipartite system to describe the system and bath. The combined state is defined by $\hat{\rho}_{SB}$ and the system state is obtained by a partial trace over the bath $\hat{\rho}_S = \text{Tr}_B\{\hat{\rho}_{SB}\}$.

There is a hierarchy of correlation relations between the system and the bath. We adopt a concentric approach where the outermost boundary has no system-bath correlation and therefore can be described as a tensor product $\hat{\rho}_{SB} = \hat{\rho}_S \otimes \hat{\rho}_B$. This is also a classical boundary since all system observables can be measured simultaneously with bath observables. External time dependent driving can be considered as a classical limit of an interaction with a quantum field.

The next level of system-bath correlation is classical meaning that global observables can be measured simultaneously with local observables $[\hat{\rho}_{SB}, \hat{\rho}_S \otimes \hat{\mathbf{1}}_B] = 0$. Finally, we consider quantum correlation or entanglement.

The approach adopted is to telescope i.g., partitioning the system bath scenario starting from the outer boundary (cf. Fig. 1).

II. THE MARKOVIAN MASTER EQUATION AND ISOTHERMAL PARTITION

The quantum description adopts the assumption that the entire world is a large closed system and, therefore, time evolution is governed by a unitary transformation generated by a global Hamiltonian. For the combined system bath scenario, the global Hamiltonian can be decomposed into

$$\hat{\mathbf{H}} = \hat{\mathbf{H}}_S + \hat{\mathbf{H}}_B + \hat{\mathbf{H}}_{SB}, \quad (8)$$

where $\hat{\mathbf{H}}_S$ is the system's Hamiltonian, $\hat{\mathbf{H}}_B$ is the bath Hamiltonian, and $\hat{\mathbf{H}}_{SB}$ is the system-bath interaction. The state of the system at time t becomes $\hat{\rho}_S(t) = \text{Tr}_B\{\hat{\rho}_{SB}(t)\} = \text{Tr}_B\{\hat{\mathbf{U}}_t\hat{\rho}_{SB}(0)\hat{\mathbf{U}}_t^\dagger\}$, where $\hat{\mathbf{U}}_t$ is generated by the total Hamiltonian $\hat{\mathbf{U}}_t = e^{-\frac{i}{\hbar}\hat{\mathbf{H}}t}$.

Reduced dynamics is a dynamical procedure concentrating only on system observables therefore utilizing system operators. An important assumption is that at $t = 0$ the system and bath are uncorrelated

$$\hat{\rho}_{SB}(0) = \hat{\rho}_S(0) \otimes \hat{\rho}_B(0). \quad (9)$$

This assumption can be moved to $t \rightarrow -\infty$ and will be scrutinized later.

Assuming unitary dynamics generated by the total Hamiltonian (8) and starting from an uncorrelated initial system-bath state [Eq. (9)], the reduced map $\Lambda_S(t)$ has the structure

$$\hat{\rho}_S(t) = \Lambda_S(t)\hat{\rho}_S(0) = \sum_j \hat{\mathbf{K}}_j(t)\hat{\rho}_S(0)\hat{\mathbf{K}}_j^\dagger(t), \quad (10)$$

where $\hat{\mathbf{K}}$ are system operators and $\sum_j \hat{\mathbf{K}}_j\hat{\mathbf{K}}_j^\dagger = \hat{\mathbf{I}}$. This general result has been derived by Kraus¹⁴ and is termed a completely positive trace preserving (CPTP) map.

The CPTP map is contracting meaning that the distance between two states diminishes. This distance between $\hat{\rho}_1$ and $\hat{\rho}_2$ can be defined by the conditional entropy $\mathcal{S}(\hat{\rho}_1|\hat{\rho}_2) = \text{Tr}\{\hat{\rho}_1 \ln \hat{\rho}_1 - \hat{\rho}_1 \ln \hat{\rho}_2\}$. Applying the map Λ leads to a quantum version of the H-theorem,¹⁵

$$\mathcal{S}(\Lambda\hat{\rho}_A|\Lambda\hat{\rho}_B) \leq \mathcal{S}(\hat{\rho}_A|\hat{\rho}_B). \quad (11)$$

If the map has a unique fixed point $\Lambda\hat{\rho}_{st} = \hat{\rho}_{st}$, then using Eq. (11) it becomes clear that repeated applications of the map will lead monotonically to this fixed point, a mathematical property associated with thermal equilibrium.¹⁶

A differential form of the CPTP map can be obtained by imposing a Markovian and stationary property: $\Lambda_S(t+s) = \Lambda_S(t)\Lambda_S(s)$. The differential generator of the dynamics can be defined by $\Lambda_S(t) = e^{\mathcal{L}t}$ leading to the quantum master equation

$$\frac{d}{dt}\hat{\rho}_S = \mathcal{L}\hat{\rho}_S. \quad (12)$$

An important milestone was the derivation of the most general form of the generator of Markovian dynamics by Gorini-Kossakowski-Lindblad-Sudarshan (GKLS).^{17,18} The differential generator \mathcal{L} of the map becomes

$$\frac{d}{dt}\hat{\rho}_S = (\mathcal{L}_H + \mathcal{L}_D)\hat{\rho}_S = -\frac{i}{\hbar}[\hat{\mathbf{H}}_S, \hat{\rho}_S] + \sum_j \left(\hat{\mathbf{L}}_j\hat{\rho}_S\hat{\mathbf{L}}_j^\dagger - \frac{1}{2}\{\hat{\mathbf{L}}_j^\dagger\hat{\mathbf{L}}_j, \hat{\rho}_S\} \right), \quad (13)$$

where $\hat{\mathbf{L}}$ are system jump operators and $\hat{\mathbf{H}}_S$ is a renormalized system Hamiltonian.

The dynamics generated by the GKLS form (13) based on Kraus mapping [Eq. (10)] implies a tensor product form between the system and bath at all times $\hat{\rho}_{SB}(t) = \hat{\rho}_S(t) \otimes \hat{\rho}_B(t)$. This structure is equivalent to a partition between the system and bath. All system observables are defined by the system state $\hat{\rho}_S$: $\langle \hat{\mathbf{A}} \rangle = \text{Tr}\{\hat{\mathbf{A}}\hat{\rho}_S\}$.

The GKLS equation describes irreversible dynamics with positive entropy production leading to a fixed point^{19,20}

$$\frac{d}{dt}\mathcal{S}(\hat{\rho}(t)|\hat{\rho}_{st}) = -\text{Tr}[\mathcal{L}\hat{\rho}(t)(\ln \hat{\rho}(t) - \ln \hat{\rho}_{st})] \geq 0, \text{ for } \mathcal{L}\hat{\rho}_{st} = 0, \quad (14)$$

where the fixed point for the dynamics is $\hat{\rho}_{st}$.

The formal mathematical structure of CPTP maps and the GKLS master equation leave open the choice of the Hamiltonian $\hat{\mathbf{H}}_S$ and the jump operators $\hat{\mathbf{L}}$ in Eq. (13). We will employ this structure to define the outermost boundary between the system and bath (cf. Sec. IX B).

III. THE BORN-MARKOV WEAK COUPLING APPROXIMATION

A constructive approach to derive the GKLS master equation from first principles is desirable allowing us to address directly physical reality. The method known as Davies construction²¹ is based on a second order expansion where the small parameter λ scales the system-bath interaction

$$\hat{\mathbf{H}}_{int} = \lambda \sum_k \hat{\mathbf{S}}_k \otimes \hat{\mathbf{B}}_k, \quad (15)$$

where $\hat{\mathbf{S}}$ are system operators and $\hat{\mathbf{B}}$ are bath operators. The rigorous derivation of Davies²¹ leads to the GKLS form and has the property of thermodynamic consistency.²² The derivation is based on the weak coupling limit (WCL), which includes the heuristic ideas of Born, Markovian, and secular approximations. These techniques were previously applied to examples of open systems such as nuclear magnetic resonance by Bloch²³ and later by Redfield.²⁴ Other approaches to the open system master equation include the projection technique of Nakajima-Zwanzig.^{25,26}

A basic step in the derivation is to transform to the interaction representation generated by the free evolution $\hat{\mathbf{U}}(t) = e^{-\frac{i}{\hbar}\hat{\mathbf{H}}_S t} \otimes e^{-\frac{i}{\hbar}\hat{\mathbf{H}}_B t}$. At this point, the system coupling operators $\hat{\mathbf{S}}_k$ in Eq. (15) are expanded by eigenoperators of the free system propagator

$$\mathcal{U}_S(t)\hat{\mathbf{A}}_\omega = e^{\frac{i}{\hbar}\hat{\mathbf{H}}_S t}\hat{\mathbf{A}}_\omega e^{-\frac{i}{\hbar}\hat{\mathbf{H}}_S t} = e^{-i\omega t}\hat{\mathbf{A}}_\omega \quad (16)$$

($\{\omega\}$ denotes the set of Bohr frequencies of $\hat{\mathbf{H}}_S$). Then,

$$e^{\frac{i}{\hbar}\hat{\mathbf{H}}_S t}\hat{\mathbf{S}}_k e^{-\frac{i}{\hbar}\hat{\mathbf{H}}_S t} = \sum_{\{\omega\}} s_k(\omega)\hat{\mathbf{A}}_\omega e^{-i\omega t}. \quad (17)$$

Adding to the WCL method a renormalization procedure which allows us to use the physical Hamiltonian $\hat{\mathbf{H}}_S$ of the system, containing lowest order Lamb corrections, one obtains the following structure of the Markovian master equation which has the GKLS form:

$$\frac{d}{dt}\hat{\rho}_S = -i[\hat{\mathbf{H}}_S, \hat{\rho}_S] + \mathcal{L}_D\hat{\rho}_S, \quad \mathcal{L}_D\hat{\rho}_S = \sum_{k,l} \sum_{\{\omega\}} \mathcal{L}_{lk}^\omega \hat{\rho}_S, \quad (18)$$

where

$$\mathcal{L}_{lk}^\omega \hat{\rho}_S = \frac{1}{2\hbar^2} \tilde{R}_{kl}(\omega) s_l(\omega) s_k(\omega) \left\{ [\hat{\mathbf{A}}_\omega \hat{\rho}_S, \hat{\mathbf{A}}_\omega^\dagger] + [\hat{\mathbf{A}}_\omega, \hat{\rho}_S \hat{\mathbf{A}}_\omega^\dagger] \right\}. \quad (19)$$

The eigenoperators $\hat{\mathbf{A}}_\omega$ become the ‘‘jump’’ operators $\hat{\mathbf{L}}_j$ in the GKLS equation (13). These are eigenoperators of $\hat{\mathbf{H}}_S$, $[\hat{\mathbf{H}}_S, \hat{\mathbf{A}}_\omega] = -i\omega\hat{\mathbf{A}}_\omega$ [Eq. (16)].

The rate matrix $\tilde{R}_{kl}(\omega)$ is the Fourier transform of the bath correlation function $\langle \hat{R}_k(t)\hat{R}_l \rangle_{bath}$, computed in the thermodynamic limit

$$\tilde{R}_{kl}(\omega) = \int_{-\infty}^{+\infty} e^{i\omega t} \langle \hat{\mathbf{B}}_k(t) \hat{\mathbf{B}}_l \rangle_{\text{bath}} dt. \quad (20)$$

The derivation of (18) and (19) imposes additional thermodynamical properties of the master equation:

- (1) The Hamiltonian part $[\hat{\mathbf{H}}_S, \bullet]$ commutes with the dissipative part \mathcal{L}_D .
- (2) The diagonal (in $\hat{\mathbf{H}}_S$ -basis) matrix elements of $\hat{\rho}_S$ evolve (independent of the off-diagonal ones) according to the Pauli master equation with transition rates given by the Fermi golden rule.^{27,28}

In addition, if the bath is a heat bath,^{29,30} then

- (3) Gibbs state $\hat{\rho}_\beta = Z^{-1} e^{-\beta \hat{\mathbf{H}}_S}$ is a stationary solution of (18).
- (4) Any initial state relaxes asymptotically to the Gibbs state: *The 0-Law of Thermodynamics*.¹⁶

The derivation of (18) and (19) can be extended to describe driven systems with a time dependent system Hamiltonian $\hat{\mathbf{H}}_S(t)$. The jump operators $\hat{\mathbf{A}}_\omega$ become eigenoperators of the free time dependent propagator $\mathcal{U}_S(t)$. The adiabatic case of a slowly varying time-dependent Hamiltonian is the simplest case. The jump operators become the eigenoperators of the instantaneous propagator or $[\hat{\mathbf{H}}_S(t), \hat{\mathbf{A}}_\omega(t)] = -i\omega(t) \hat{\mathbf{A}}_\omega(t)$.³¹

A quantum dynamical version of the first law of thermodynamics is obtained by examining the energy conservation law in the adiabatic case^{22,32}

$$E(t) = \text{Tr}(\hat{\rho}_S(t) \hat{\mathbf{H}}_S(t)). \quad (21)$$

Taking the time derivative of Eq. (21) results in the change in energy partitioned to power and heat currents,

$$\frac{d}{dt} E(t) = \mathcal{J}(t) - \mathcal{P}(t), \quad (22)$$

where the power provided by the system becomes

$$\mathcal{P}(t) \equiv -\text{Tr}(\hat{\rho}_S(t) \frac{d\hat{\mathbf{H}}_S(t)}{dt}). \quad (23)$$

The heat current becomes

$$\begin{aligned} \mathcal{J}(t) &\equiv \text{Tr}(\hat{\mathbf{H}}_S(t) \frac{d}{dt} \hat{\rho}_S(t)) = \sum_k \mathcal{J}_k(t), \\ \mathcal{J}_k(t) &= \text{Tr}(\hat{\mathbf{H}}_S(t) \mathcal{L}_k(t) \hat{\rho}_S(t)). \end{aligned} \quad (24)$$

The heat is the sum of net heat currents supplied by the individual heat baths where we consider the possibility of more than one bath.

Employing the property of positive entropy production, Eq. (14)^{19,20} applied to individual generators $\mathcal{L}_k(t)$ reproduces the second law of thermodynamics in the form

$$\frac{d}{dt} S_{vn}(t) - \sum_k \frac{1}{T_k} \mathcal{J}_k(t) \geq 0, \quad (25)$$

where S_{vn} is the von Neumann entropy $S_{vn} = -\text{Tr}(\hat{\rho}_S \ln \hat{\rho}_S)$ [Eq. (25)] was obtained first for the constant $\hat{\mathbf{H}}$ in Ref. 33 and subsequently generalized in Ref. 32.

The derivation of the WCL of the GKLS has been criticized as being too strict. It has been suggested to limit the convolution integral to finite time and to obtain a non-Markovian theory. Another option is not to perform the secular approximation and obtain the Redfield equation,^{34–36} which is not CPTP. Cohen and Tannor have indicated that the GKLS equation is not consistent with the semiclassical notion of translation invariance.³⁷ From a thermodynamical perspective, only the GKLS equation is consistent.³⁸ The conditions for the validity of the weak coupling limit become the idealization which produces a consistent thermodynamical framework of a subsystem coupled isothermally to a bath.

A. Reduced dynamics under periodic and nonperiodic driving

The master equation for a time dependent Hamiltonian needs particular attention. When the driving is fast, the previous adiabatic approximation is inappropriate. The key issue in the derivation is to obtain the time dependent free propagator $\mathcal{U}_S(t)$, defined by

$$\frac{d}{dt} \mathcal{U}_S(t) = \mathcal{L}_H(t) \mathcal{U}_S(t), \quad (26)$$

where $\mathcal{L}_H = -\frac{i}{\hbar} [\hat{\mathbf{H}}_S(t), \bullet]$. In the WCL, the free propagator is employed to transform to the interaction representation. Then, the instantaneous eigenoperators of $\mathcal{U}_S(t)$,

$$\mathcal{U}_S(t) \hat{\mathbf{A}}_n = e^{-i\phi_n t} \hat{\mathbf{A}}_n, \quad (27)$$

become the jump operators in the GKLS equation.³⁹ Such a decomposition is possible in periodic and special protocols of nonperiodic driving.

The master equation for periodic modulation of the Hamiltonian $\hat{\mathbf{H}}_S(t) = \hat{\mathbf{H}}_S(t + \tau)$ is the basis for spectroscopy and control in condensed phases as well as in continuous thermodynamic devices.^{40–44} The main assumption is that modulation is fast, i.e., its frequency is comparable to the relevant Bohr frequencies of the system Hamiltonian. Employing the Floquet theory, the unitary propagator $\hat{\mathbf{U}}_S(t) \equiv \hat{\mathbf{U}}_S(t, 0)$ can be written as

$$\hat{\mathbf{U}}_S(t) = \hat{\mathbf{U}}_p(t) e^{-\frac{i}{\hbar} \hat{\mathbf{H}}_{av} t}, \quad (28)$$

where $\hat{\mathbf{U}}_p(t) = \hat{\mathbf{U}}_p(t + \tau)$ is a periodic propagator and $\hat{\mathbf{H}}_{av}$ can be called *averaged Hamiltonian*. Under similar assumptions as before, one can derive using the WCL procedure, the Floquet-Markovian Master Equation (ME) in the *interaction picture*

$$\frac{d}{dt} \hat{\rho}^{int}(t) = \mathcal{L} \hat{\rho}^{int}(t), \quad \mathcal{L} \hat{\rho} = \sum_{k,l} \sum_{\{\omega_q\}} \mathcal{L}_{lk}^{\omega_q} \hat{\rho}, \quad (29)$$

where

$$\mathcal{L}_{lk}^{\omega_q} \hat{\rho} = \frac{1}{2\hbar^2} \tilde{R}_{kl}(\omega_q) \{ [\hat{\mathbf{A}}_l(\omega_q) \hat{\rho}, \hat{\mathbf{A}}_k^\dagger(\omega_q)] + [\hat{\mathbf{A}}_l(\omega_q), \hat{\rho} \hat{\mathbf{A}}_k^\dagger(\omega_q)] \}. \quad (30)$$

Now, the summation in (29) is taken over the set of *extended Bohr frequencies* $\{\omega_q = \omega_{av} + q\Omega | \omega_{av} - \text{Bohr frequencies of } \hat{\mathbf{H}}_{av}, q \in \mathbf{Z}\}$, which take into account the exchange processes of energy quanta $\hbar|q|\Omega$ with the source of external modulation.

Heat currents corresponding to different baths can be defined for any time. As a result, the second law [Eq. (14)] is satisfied for this definition. The definition of the first law is intricate. For fast modulation, the instantaneous decomposition of energy into work and internal energy of the system is ambiguous. Only in the limit cycle, where the system's internal energy and entropy are constant and the heat currents are time independent, we can write the first law employing the average energy conservation. The heat currents associated with the j bath are given in terms of the corresponding interaction picture generator

$$\mathcal{J}_j = \sum_{l,k \in I_j} \sum_{\{\omega_q\}} \frac{\omega_q}{\omega_{av}} \text{Tr}(\hat{\mathbf{H}}_{av} \mathcal{L}_{lk}^{\omega_q} \hat{\rho}_0), \quad (31)$$

and I_j denotes the subset of indices corresponding to the interaction with the j th heat bath. The power is defined by the energy conservation,

$$\mathcal{P} = \sum_j \mathcal{J}_j. \quad (32)$$

The second law becomes the sum of entropy productions in the baths,

$$\sum_j \frac{1}{T_j} \mathcal{J}_j \leq 0. \quad (33)$$

B. Driving protocol with slow acceleration

A general approach to time dependent driven systems is possible if an explicit solution can be found for the free propagator $\mathcal{L}_S(t)$. For this to occur, the Hamiltonian $\hat{\mathbf{H}}_S(t)$ has to be decomposed within elements of a Lie algebra. Consider a closed set of operators $\{\hat{\mathbf{G}}\}$ which are elements of a Lie algebra

$$[\hat{\mathbf{G}}_j, \hat{\mathbf{G}}_i] = \sum_{k=1}^N c_k^{ij} \hat{\mathbf{G}}_k, \quad (34)$$

where c_k^{ij} are the structure constants.

If the Hamiltonian $\hat{\mathbf{H}}_S(t)$ is also a member of the algebra, it can be decomposed as a linear combination of the operators $\{\hat{\mathbf{G}}\}$,

$$\hat{\mathbf{H}}_S(t) = \sum_{j=1}^N h_j(t) \hat{\mathbf{G}}_j. \quad (35)$$

With the help of the identity equation (35), one concludes that the equations of motion for the system operators are closed under the Lie algebra.⁴⁵

The eigenoperators can be found by representing the dynamics in Liouville space (known also as Hilbert-Schmidt space).⁴⁶ In the Liouville representation, the system's dynamics are represented in terms of a chosen basis of operators spanning the Liouville space (such as $\{\hat{\mathbf{G}}\}$). This basis of operators constructs a vector $\vec{v}(t)$ in observable space.

Employing the Heisenberg equation of motion, the dynamics of \vec{v} is given by

$$\frac{d}{dt} \vec{v}(t) = \left\{ \frac{i}{\hbar} [\hat{H}(t), \bullet] + \frac{\partial}{\partial t} \right\} \vec{v}(t). \quad (36)$$

Here, we consider a finite basis of size N , which also forms a closed Lie algebra. This guarantees that the Heisenberg equations of motion (36) can be solved within the basis,⁴⁵ implying that Eq. (36) can be represented in a vector matrix form

$$\frac{d}{dt} \vec{v}(t) = \mathcal{G}(t) \vec{v}(t), \quad (37)$$

where $\mathcal{G}(t)$ is an N by N matrix and \vec{v} is an N -dimensional vector. The task to find the eigenvalue solution of Eq. (38) is hindered by the explicit time dependence of $\mathcal{G}(t)$. If by a proper choice of a time dependent operator base and a driving protocol, the time dependence can be concentrated to $\mathcal{G}(t) = \Omega(t)\mathcal{B}$, then⁴⁷

$$\frac{d}{d\theta} \vec{v}(\theta) = \mathcal{B} \vec{v}(\theta), \quad (38)$$

where $\theta = \int \Omega dt$ is a scaled time. The eigenvectors of the propagator can be obtained by diagonalizing \mathcal{B} . We can follow the ideas of the adiabatic theorem meaning that even if \mathcal{B} has a slow time dependence, its eigenoperators will follow the evolution with an accumulated phase

$$\mathcal{B} \vec{A}_j = e^{i\lambda_j(\theta)} \vec{A}_j. \quad (39)$$

From Eq. (39), the time dependent eigenoperator $\hat{\mathbf{A}}_j$ can be reconstructed from the basis operators of the algebra $\{\hat{\mathbf{G}}\}$.

The jump operators are eigenoperators of the free evolution obeying Eq. (39). They form a complete basis within the system's algebra. If the operator $\hat{\mathbf{S}}_k$ [Eq. (46)] is also an element of the Lie algebra, it can be expanded in the interaction representation in terms of the set $\{\hat{\mathbf{A}}_j(t)\}$,

$$\tilde{\mathbf{S}}_k(t) = \sum_j \chi_j^k(t) \hat{\mathbf{A}}_j(t). \quad (40)$$

The coefficients $\chi_j^k(t)$ are, in general, complex and can be written in a polar representation leading to the desired form $\tilde{\mathbf{S}}_k(t) = \sum_j \xi_j^k(t) e^{i\theta_j^k(t)} \hat{\mathbf{A}}_j$. Here, $\xi_j^k(t) = |\chi_j^k(t) \cdot \lambda_j(t)|$ and $\theta_j^k(t) = \phi_j(t) + \arg(\lambda_j(t))$.

The result is a GKLS master equation with time dependent operators and rate coefficients³⁹ shown in the interaction representation

$$\begin{aligned} \frac{d}{dt} \tilde{\rho}_S(t) = & -i[\hat{\mathbf{H}}_{LS}(t), \tilde{\rho}_S(t)] \\ & + \sum_j \gamma_j(\alpha_j(t)) (\hat{\mathbf{A}}_j \tilde{\rho}_S(t) \hat{\mathbf{A}}_j^\dagger - \frac{1}{2} \{ \hat{\mathbf{A}}_j^\dagger \hat{\mathbf{A}}_j \tilde{\rho}_S(t) \}), \end{aligned} \quad (41)$$

where $\hat{\mathbf{H}}_{LS}(t)$ is an addition to the Hamiltonian known as the Lamb shift. The rate coefficients γ_j depend on a renormalized system frequency $\alpha \neq \omega$ which depends on the driving speed. In addition, unlike the stationary WCL [Eq. (18)], energy and coherence are mixed.³⁹

The time dependent GKLS master equation with a time dependent protocol for $\hat{\mathbf{H}}_S(t)$ [Eq. (41)] allows the study of shortcuts to isothermal processes.⁴⁸ The task is to find a protocol starting from a thermal initial state $\hat{\rho}_i = e^{-\beta \hat{\mathbf{H}}_i} / Z$ will result in a thermal final state with a different Hamiltonian $\hat{\rho}_f = e^{-\beta \hat{\mathbf{H}}_f} / Z$. The fast protocols found

overshoot the energy scale of \hat{H}_i and \hat{H}_f at intermediate times. What is unique in this process is that they involve a shortcut to a process with entropy change.

IV. THE REPEATED COLLISION MODEL

The collision model originated to describe the dynamics of a particle colliding with the background gas particles.^{23,49} Using the assumption of rare uncorrelated collisions, a Poissonian process can be used to model the encounters, a quantum version of the Boltzmann equation.⁵⁰ It is assumed that the system and j gas particle are initially uncorrelated $\hat{\rho}_i = \hat{\rho}_{S_i} \otimes \hat{\rho}_{B_j}$. The individual collision event is then described by a unitary scattering matrix \hat{S} ,

$$\hat{\rho}_f = \hat{S} \hat{\rho}_i \hat{S}^\dagger. \quad (42)$$

Assuming independent random collisions with identical bath particles, a reduced map is obtained

$$\hat{\rho}_{S_j} = \Lambda_\beta \hat{\rho}_{S_i} = \text{Tr}_B \{ \hat{\rho}_f \}. \quad (43)$$

To generalize to many recurrent encounters at rate γ , the collision duration has to be much faster than the average waiting time between collisions $\sim 1/\gamma$. The differential description leads to a GKLS master equation^{51,52}

$$\frac{d}{dt} \hat{\rho}_S = -\frac{i}{\hbar} [\hat{H}_S, \hat{\rho}_S] + \gamma \left(\text{Tr}_B \{ \hat{S} \hat{\rho}_S \otimes \hat{\rho}_B \hat{S}^\dagger \} - \hat{\rho}_S \right). \quad (44)$$

The repeated collision GKLS equation (44) depends on the bath state. A natural choice is a bath in thermal equilibrium $\hat{\rho}_B = \frac{1}{Z} \exp\{-\beta \hat{H}_B\}$.

As in any CPTP map, the collision dynamics leads to a fixed point $\mathcal{L} \hat{\rho}_{st} = 0$. This model raises an interesting issue concerning the irreversibility of the process. If we follow the collision process and keep track of every colliding atom before and after the collision, the process is unitary and therefore, in principle, reversible. The system and bath particles due to the collision encounter become entangled. The loss of this bipartite mutual information is the source of entropy production. Irreversibility can be traced to the loss of record or timing of the individual collision events.⁵³

For modeling, it would be desirable that this fixed point is a thermal equilibrium state of the system $\hat{\rho}_S = \frac{1}{Z} \exp(-\beta \hat{H}_S)$. To study this possibility, the unitary scattering matrix \hat{S} can be described by a Hermitian generator \hat{V} and then $\hat{S} = e^{-\frac{i}{\hbar} \hat{V} \phi}$, where ϕ is a phase shift.

The master equation (44) can be expanded to second order in ϕ leading to⁵⁴

$$\frac{d}{dt} \hat{\rho}_S = -\frac{i}{\hbar} [\hat{H}'_S, \hat{\rho}_S] - \gamma' \text{Tr}_B \{ [\hat{V}, [\hat{V}, \hat{\rho}_S \otimes \hat{\rho}_B]] \}, \quad (45)$$

where $\gamma' = \gamma \frac{\phi^2}{2\hbar^2}$ and $\hat{H}'_S = \hat{H}_S + \gamma \frac{\phi}{\hbar} \text{Tr}_B \{ \hat{V} \}$.

To obtain a thermalizing model, we can choose \hat{V} as follows:⁵⁵⁻⁵⁹

$$\hat{V} = \sum_k g_k (\hat{A}_k^\dagger \otimes \hat{B}_k + \hat{A}_k \otimes \hat{B}_k^\dagger), \quad (46)$$

where \hat{A}_k and \hat{B}_k are eigenoperators of the commutators of the free Hamiltonians with the same eigenvalue,

$$[\hat{H}_S, \hat{A}_k] = -\omega_k \hat{A}_k, \quad (47)$$

$$[\hat{H}_B, \hat{B}_k] = -\omega_k \hat{B}_k.$$

As a result, the operator \hat{V} commutes with $[\hat{H}_S + \hat{H}_B, \hat{V}] = 0$. Using these properties, Eq. (45) reduces to a thermalizing GKLS master equation

$$\frac{d}{dt} \hat{\rho}_S = -\frac{i}{\hbar} [\hat{H}_S, \hat{\rho}_S] - \sum_k (\gamma_k^- \mathcal{L}_k^- (\hat{\rho}_S) + \gamma_k^+ \mathcal{L}_k^+ (\hat{\rho}_S)), \quad (48)$$

where $\mathcal{L}_k^- (\hat{\rho}_S) = [\hat{A}_k \hat{\rho}_S, \hat{A}_k^\dagger] + [\hat{A}_k, \hat{\rho}_S \hat{A}_k^\dagger]$ and $\mathcal{L}_k^+ (\hat{\rho}_S) = [\hat{A}_k^\dagger \hat{\rho}_S, \hat{A}_k] + [\hat{A}_k^\dagger, \hat{\rho}_S \hat{A}_k]$. The rate coefficients obey

$$\gamma_k^- = \gamma' g_k^2 \langle \hat{B}_k \hat{B}_k^\dagger \rangle, \quad (49)$$

$$\gamma_k^+ = \gamma' g_k^2 \langle \hat{B}_k^\dagger \hat{B}_k \rangle.$$

When the bath is in thermal equilibrium, the ratio of rate coefficients obeys detailed balance

$$\frac{\gamma_k^+}{\gamma_k^-} = e^{-\beta \omega_k}. \quad (50)$$

This concludes the derivation of a thermalizing GKLS collision model.

Although the physical motivation for the weak coupling limit and the repeated collision model is different, the mathematical structure has many similarities.⁶⁰ In addition, the form of \hat{V} in Eq. (46) will also lead to thermal equilibrium for strong collisions where ϕ is large since \hat{S} in Eq. (44) commutes with the Hamiltonian $[\hat{S}, \hat{H}_S + \hat{H}_B] = 0$ leading to $[\hat{S}, \hat{\rho}_{SB}] = \frac{1}{Z} [\hat{S}, e^{-\beta \hat{H}_S} \otimes e^{-\beta \hat{H}_B}] = 0$; therefore, $\hat{\rho}_{SB}$ is a fixed point of the CPTP map in Eq. (42).^{56,61} In quantum thermodynamics resource theory, this map is known as a thermal map.^{62,63}

V. THE GAUSSIAN SEMIGROUP: THE SINGULAR BATH LIMIT

An extreme case is a system subject to random uncorrelated kicks from the environment. We expect in analogy to the central limit theorem that the accumulated environmental influence will attain a limit. The process is one sided since the system does not exert back action on the environment. This process can be viewed as a quantum version of Langevin dynamics described by

$$\dot{\hat{H}} = \hat{H}_S + \hat{V} f(t), \quad (51)$$

where the random force typically $\langle f(t) \rangle = 0$ and $\langle f(t) f(t') \rangle = \gamma \delta(t - t')$. Such a process leads to a GKLS equation when averaging over the random noise^{64,65}

$$\frac{d}{dt} \hat{\rho}_S = -\frac{i}{\hbar} [\hat{H}_S, \hat{\rho}_S] - \frac{\gamma^2}{2} [\hat{V}, [\hat{V}, \hat{\rho}_S]]. \quad (52)$$

Equation (52) is known as the generator of a Gaussian semigroup.¹⁷ A physical interpretation is the accumulation of many small uncorrelated perturbations also obtained in the limit of interaction with a bath of infinite temperature. Notice that the entropy exchange with

such a bath is zero. Another interpretation of Eq. (52) is a system's evolution undergoing a weak continuous quantum measurement of the observable $\langle \hat{V} \rangle$.^{66–68}

The phenomenon most associated with Gaussian noise is dephasing. If we choose $\hat{V} = g(\hat{\mathbf{H}}_S)$, where $g(x)$ is any analytical function of X , then Eq. (52) conserves energy and the dissipation causes dephasing. In the terminology of magnetic resonance a pure T_2 process.⁶⁹

Pure dephasing will also occur if the \hat{S} matrix in the scattering event [Eq. (44)] commutes with $\hat{\mathbf{H}}_S$: $[\hat{\mathbf{H}}_S, \hat{S}] = 0$. The Poisson dephasing due to repeated collision, in the limit of small action [Eq. (45)], becomes equivalent to the Gaussian dephasing model with the same \hat{V} . Nevertheless, when the action is large $\phi \sim 1$, the Poissonian and Gaussian models of dephasing become different.⁷⁰ In Gaussian dephasing, the high order coherences are eliminated faster than nearest neighbor coherences. Poisson-type dephasing can reach a limit where all coherences are eliminated at the same rate. Experimental evidence for vibrational dephasing of I_3^- in solution indicates a Poissonian mechanism.⁷⁰

VI. THE LAWS OF QUANTUM THERMODYNAMICS

An integral part of the development of a numerical simulation are schemes to test the validity of the approximation. Comparing the quantum simulation results to thermodynamic predictions serves such a critical test. Quantum mechanics and thermodynamics are two separate theories which means that thermodynamics can serve as an external criterion to verify the validity of our quantum simulations.²²

A. The zero law

Dynamically the zero law of thermodynamics states that any system with Hamiltonian $\hat{\mathbf{H}}_S$ will eventually reach a steady state of the dynamics with a final fixed point $\hat{\rho}_{st} = \frac{1}{Z} \exp(-\beta \hat{\mathbf{H}}_S)$. An equivalent statement is that $\hat{\rho}_{st}$ is an invariant of the dynamics $\Lambda \hat{\rho}_{st} = \hat{\rho}_{st}$ with eigenvalue 1. We therefore expect the dynamical simulations of an open system to lead to a fixed point. An exception is a bifurcation point which can be identified by a degenerate eigenvalue of the dynamical map with the value of 1. Such a non-Hermitian point is termed an exceptional point⁷¹ (cf. Subsection VII B).

B. The I-law

The I-law addresses the issue of conserved quantities. The primary quantity is the total energy. An additional variable important in transport is the number of particles.

To obtain the conservation laws in a differential form, we can write the equations of motion in the Heisenberg form

$$\frac{d}{dt} \hat{\mathbf{X}} = -\frac{i}{\hbar} [\hat{\mathbf{H}}_S, \hat{\mathbf{X}}] + \mathcal{L}_S(\hat{\mathbf{X}}) + \frac{\partial}{\partial t} \hat{\mathbf{X}}, \quad (53)$$

where $\hat{\mathbf{X}}$ is a system operator which can be explicitly time dependent. Choosing for $\hat{\mathbf{X}}$ the Hamiltonian $\hat{\mathbf{H}}_S$, using the fact that $\hat{\mathbf{H}}$ commutes with itself, and taking expectation values, we obtain

$$\frac{d}{dt} E = \langle \mathcal{L}_D^*(\hat{\mathbf{H}}_S) \rangle + \left\langle \frac{\partial}{\partial t} \hat{\mathbf{H}}_S \right\rangle, \quad (54)$$

which leads to the interpretation $\mathcal{J} = \dot{Q} = \langle \mathcal{L}_D^*(\hat{\mathbf{H}}_S) \rangle$ as heat current and $\mathcal{P} = \langle \frac{\partial}{\partial t} \hat{\mathbf{H}}_S \rangle$ as power. This dynamical version of the I-law [Eq. (54)] is equivalent to Eq. (25) obtained in the Schrödinger frame and is limited to the adiabatic regime.^{22,72}

In the nonadiabatic regime or in strong system bath coupling, the simple partition between heat and work loses its meaning.⁷³ Work is required to generate coherence, but at later times this work can potentially be extracted as work or dissipated as heat.⁷⁴

In quantum dynamics the definition of work is ambiguous. The classical analog requires two energy measurements.⁷⁵ As a result, the measurement influences the outcome erasing coherence.^{76–78}

C. The II-law

The Clausius statement for the II-law is that heat should flow through the system from a hot to a cold bath.⁷⁹ An alternative version, due to Kelvin, can be stated as the universal tendency in nature to dissipate mechanical energy.⁸⁰ Both these criteria can be employed directly to assess open system models.

The Clausius version of the II-law can be employed as a test for the quantum heat transport problem of two connected quantum systems coupled to a hot and cold bath. The dynamics can be described by

$$\frac{d}{dt} \hat{\rho} = -\frac{i}{\hbar} [\hat{\mathbf{H}}_0 + \hat{\mathbf{H}}_{hc}, \hat{\rho}] + \mathcal{L}_h(\hat{\rho}) + \mathcal{L}_c(\hat{\rho}), \quad (55)$$

where the wire Hamiltonian is $\hat{\mathbf{H}}_0 = \hat{\mathbf{H}}_h + \hat{\mathbf{H}}_c$, $\hat{\mathbf{H}}_{hc}$ is the link Hamiltonian, and $\mathcal{L}_{h/c}$ are the dissipative connections to the hot and cold baths. In constructing such a model, it is tempting to assign a local thermalizing GKLS generator to each subsystem and then to introduce a weak coupling term connecting the two subsystems. In this case, the jump operators in \mathcal{L}_h are the eigenoperators of $\hat{\mathbf{H}}_h$ and for \mathcal{L}_c are the eigenoperators of $\hat{\mathbf{H}}_c$.

The global alternative is to use the full power of the Davies construction (cf. Sec. III) and find the eigenoperators of $\hat{\mathbf{H}}_S$ to construct both generators \mathcal{L}_h and \mathcal{L}_c .⁸¹

At steady state, the heat flow from the hot (cold) bath is given by

$$\mathcal{J}_{h(c)} = \text{Tr}\{(\mathcal{L}_{h(c)} \hat{\rho}_s)(\hat{\mathbf{H}}_0 + \hat{\mathbf{H}}_{hc})\}, \quad (56)$$

where $\hat{\rho}_s$ is the steady state density operator.

In the local approach, it is assumed that the intersystem coupling does not affect the system bath coupling. Therefore, in the derivation of the master equation, the internal coupling Hamiltonian $\hat{\mathbf{H}}_{hc}$ is ignored. The heat current becomes⁸¹

$$\mathcal{J}_h = (e^{\beta_c \omega_c} - e^{\beta_h \omega_h}) \mathcal{F}, \quad (57)$$

where \mathcal{F} is a function of the coupling constants, which is always positive irrespective of the in-balance of the coupling constants. The Clausius statement for the second law of thermodynamics implies that heat cannot flow from a cold body to a hot body without external work being performed on the system. It is apparent from Eq. (57) that the direction of heat flow depends on the choice of parameters. For $\frac{\omega_c}{T_c} < \frac{\omega_h}{T_h}$, heat will flow from the cold bath to the hot bath; thus, the second law is violated even at vanishing small h - c coupling.

The global approach to the GKLS equation derives the master equation using the Davies WCL procedure with the global Hamiltonian $\hat{H}_S = \hat{H}_h + \hat{H}_c + \hat{H}_{hc}$. This form is consistent with the II-law,⁸¹ except when the two subsystems are in resonance. The reason is the violation of the secular approximation.^{82,83} The collision model⁵⁷ allows another perspective of this violation. Considering the local master equation derived from the collision approach [Eq. (48)], the local approach will violate the II-law. A possible remedy for this discrepancy is to add the cost of work to switch on and off the system bath interaction.

The Kelvin version of the II-law can also be employed directly in testing the consistent description of a driven system coupled to a bath.⁴⁰ The most elementary model is a driven qubit or two-level-system (TLS) coupled to a bath

$$\hat{H}_S(t) = \hat{H}_0 + \hat{W}(t),$$

where

$$\hat{H}_0 = \omega \hat{\sigma}_z \quad (58)$$

and

$$\hat{W}(t) = 2\epsilon (\hat{\sigma}_x \cos(\nu t) + \hat{\sigma}_y \sin(\nu t)),$$

where the driving $\hat{W}(t)$ is in the rotating frame. The local master equation is constructed to equilibrate \hat{H}_0 . The result is the well-known Bloch equation.⁸⁴ Surprisingly, it violates the II-law.⁴⁰ A consistent equation with thermodynamics is obtained when deriving the master equation using the Floquet theory [Eq. (30)].

A similar violation of the II-law is obtained if one ignores the external driving in the derivation of the equation of motion for the 3-level amplifier.⁸⁵

A more general dynamical version of the II-law of thermodynamics can be used as a consistency check. It states that for an isolated system, the rate of entropy production is non-negative.²² For a typical quantum system, the second law can be expressed as

$$\frac{d}{dt} \Delta S^u = \frac{dS_{int}}{dt} + \frac{dS_m}{dt} - \sum_i \frac{\mathcal{J}_i}{T_i} \geq 0, \quad (59)$$

where \dot{S}_{int} is the rate of entropy production due to internal processes, expressed by the von Neumann entropy. \dot{S}_m is the entropy flow associated with matter entering the system, and the last term is the contribution of heat flux, \mathcal{J}_i , from the reservoir i .

D. The III-law

The third law is an additional test on the dynamics. First, it requires that the system and bath have a ground state. Dynamically, there are two independent formulations of the third law. The first, known as the Nernst heat theorem, implies that the entropy flow from any substance at absolute zero is zero.

The second formulation of the third law is a dynamical one, known as the unattainability principle: No refrigerator can cool a system to absolute zero temperature at finite time. This formulation is more restrictive than the Nernst heat theorem and imposes limitations on the spectral density and the dispersion law of the heat bath.⁴²

Note that the system can reach the ground state only if the system-bath coupling vanishes and $\hat{\rho} = \hat{\rho}_S \otimes \hat{\rho}_B$. Otherwise, at zero temperature, the system and bath are entangled.

A III-law violation in a dynamical description indicates a problem.⁸⁶ The problem can be a nonphysical spectral density or a problem in the model used to construct the master equation.

VII. THERMALIZATION

A. Eigenvalue thermalization hypothesis

Considering a finite quantum system: What are the properties that it can serve as a bath? How large does it have to be? What should be its spectrum? How should it couple to the system? Does the system bath dynamics mimic the Markovian GKLS dynamics?

Thermalization can be described as a process where the system loses its memory partly or completely of its initial state and the system settles to a steady state. In classical mechanics, chaotic dynamics even in a finite system are sufficient to lead to thermalization. On the contrary, an isolated quantum system has a discrete spectrum and therefore its dynamics is quasiperiodic. Thus, strictly speaking in terms of positive Kolmogorov entropy, isolated quantum systems are nonchaotic.⁸⁷ We therefore should search for another generic quantum property to lead to thermalization.

The eigenvalue thermalization hypothesis (ETH) originally by von Neumann⁸⁸ has been suggested as a framework for thermalization.^{89,90} ETH applies for strongly coupled quantum systems which therefore possess a repulsive Wigner-Dyson distribution of energy gaps.⁹¹ The conjecture is that the expectation value of an operator \hat{A} in the bulk of the spectrum $|E_m\rangle$ of \hat{H} , $\langle \hat{A}_M \rangle = \langle E_m | \hat{A} | E_m \rangle$, will approach asymptotically to its canonical value⁹²

$$\left| \langle \hat{A}_M \rangle - \text{Tr} \{ \hat{A} e^{-\beta(E_m)\hat{H}} / Z \} \right| \in \mathcal{O}(1/N), \quad (60)$$

where E_m is the energy of the state, $\beta(E_m)$ is the inverse temperature corresponding to the mean energy E_m , and N is the size of Hilbert space. The ETH hypothesis has been extensively tested numerically and has been found to apply in sufficiently large and complex systems.⁹²⁻⁹⁶

The ETH implies thermalization for a system coupled to a large but finite bath since the system operators are highly degenerate in the combined system. In such a case, we expect the ETH to hold^{97,98} and the system to relax to thermal equilibrium associated with the combined system-bath Hamiltonian.

B. Exceptional points

The dynamics leading to steady state is reflected by the spectrum of the generator \mathcal{L} or the propagator $\mathcal{U} = e^{\mathcal{L}t}$. The existence of an invariant or steady state $\mathcal{U}\hat{\rho}_{st} = \hat{\rho}_{st}$ means that we have an eigenvalue of 1 for the propagator and 0 for \mathcal{L} . The other eigenvalues of \mathcal{U} can be complex and are always smaller than one, $|\lambda_n| \leq 1$. There is a possibility that for certain parameters of the problem, some of the eigenvalues are degenerate. Since \mathcal{U} is not unitary and \mathcal{L} is not Hermitian, these eigenvalues are complex. Such complex degeneracies are known as exceptional points with the additional property that the associated eigenvectors coalesce.⁹⁹

This degeneracy can be either in the eigenvalue $\lambda_0 = 1$ where it means a bifurcation point or the other eigenvalues $|\lambda| < 1$ which mean a change in the dynamics. Such a degeneracy can be found in

the Bloch equation,^{84,100} where both second order and third order degeneracies were found. The degeneracy map indicates a boundary between damped and over-damped dynamics.

VIII. STRONG SYSTEM BATH COUPLING AND NON-MARKOVIAN DYNAMICS

When the system-bath coupling becomes strong, the tensor product partition is lost $\hat{\rho}_{SB} \neq \hat{\rho}_S \otimes \hat{\rho}_B$. The almost universal remedy to this problem is to move the system-bath boundary into the bath incorporating in the system a section of the bath. This is the notion of telescoping, adding an explicit primary bath layer before the final tensor product partition with the secondary bath. It is then assumed that the interface between the primary and the secondary bath is weak allowing the employment of the GKLS equation for the interface dynamics. This concept is the base of the Stochastic Surrogate Hamiltonian (SSH) method.¹⁰¹ This is also the idea behind the Driven Liouville von Neumann (DLvN) approach.¹⁰² The implementation of the two methods is different: the SSH is formulated in a stochastic wavefunction representation, while the DLvN is formulated in Liouville space. Convergence can be tested by moving the new boundary, repeating the calculation, and checking that the system observables converge.

A related approach to non-Markovian dynamics is by employing the stochastic Liouville von Neuman equation.^{103–105} For linear coupling to the bath, a quantum stochastic unraveling of the bath memory is possible.

An important consequence of moving the system-bath boundary is that non-Markovian effects are incorporated by the portion of the bath treated explicitly.

In a general stochastic process when the memory of the past decays exponentially, there is a well-studied solution which is to include memory terms in the description resulting in a Markovian description allowing a differential description embedded in a larger variable space. A quantum version is known as the Hierarchical Equation of Motion (HEOM).^{106–111} For the HEOM to work, the memory has to have exponential decay which implies decomposition to a sum of Lorentzians or to a Chebychev expansion.¹¹² A stochastic wavefunction realization of the HEOM has been developed.¹¹³

Another possibility to incorporate the bath in the system is achieved by the polaron transformation.^{114,115} This procedure is limited to a harmonic bath and a simple system Hamiltonian.

A tensor network is based on representing mixed quantum states in a locally purified form, which guarantees that positivity is preserved at all times. The approximation error is controlled with respect to the trace norm. Hence, this scheme overcomes various obstacles of the known numerical open-system evolution schemes.^{116,117}

A strong system-bath coupling leads to the dilemma of how to account for the system energy. A common suggestion is to include half of the interaction energy in the system energy $\hat{H}'_S = \hat{H}_S + \frac{1}{2}\hat{H}_{SB}$.¹¹⁸ The definition has been criticized as inconsistent.¹¹⁹

IX. THE STOCHASTIC SURROGATE HAMILTONIAN METHOD

Moving the system-bath boundary to incorporate explicitly part of the bath in the system still leaves open the choice of the

bath model. The desire is that system observables $\langle \hat{S} \rangle = \text{Tr}\{\hat{\rho}_S \hat{S}\}$ are unaffected by this choice. The freedom to choose a bath model is related to the idea of quantum simulation.¹²⁰ A system with a universal Hamiltonian can simulate the dynamics of any other quantum system, in particular, our bath.

A. Surrogate bath

We define a surrogate bath as a finite bath that represents faithfully the external influence on the system and converges to the correct open system dynamics when the size of the surrogate bath increases to infinity. A finite bath can be characterized by its energy spectrum, its bandwidth ω_{max} , and spectral density $\Delta\omega$. The bandwidth ω_{max} limits the fastest time scale $\tau_{min} \leq \frac{1}{\omega_{max}}$. For a finite time simulation with duration t_{fin} , the system cannot resolve the full spectrum of the bath. As a result, a sparse bath with a frequency spacing $\Delta\omega \geq 1/t_{fin}$ is sufficient to faithfully describe the system-bath dynamics up to time t_{fin} .

There are two leading bath models, the harmonic bath and spin bath. The two models differ in their spectral and dynamical properties.

1. Harmonic bath

The Harmonic bath is based on a normal mode decomposition of the bath Hamiltonian¹²¹

$$\hat{H}_B = \hbar \sum_k \omega_k \hat{\mathbf{b}}^\dagger \hat{\mathbf{b}}, \quad (61)$$

where, in principle, the sum runs over an infinite number of normal modes. This construction has a semiclassical origin assuming that for limited bath excitation a harmonic description is sufficient. For a bath composed of electromagnetic modes in a cavity, this bath description is exact.¹²²

A particular special solvable case is when the system bath coupling is linear in the bath modes

$$\hat{H}_{SB} = \sum_k \hat{S}_k \otimes (a\hat{\mathbf{q}}_k + b\hat{\mathbf{p}}_k), \quad (62)$$

where the coupling can be a composition of coordinate or momentum coupling. This linear bath Hamiltonian can be integrated out and summarized by an influence functional^{123,124} or by a spectral function $J(\omega)$ which incorporates the density of states and the system bath coupling.^{125,126}

An important solvable model is when the system Hamiltonian \hat{H}_S can also be decomposed to harmonic oscillators linearly coupled to the harmonic bath. In this case, the operator algebra of the system-bath is closed. There are six operators per mode; therefore, solving the dynamics means solving $6 \times (M + N)$ coupled differential equations for M system modes and N bath modes. A related solvable model is composed of N baths [Eq. (61)], each coupled to the transition between an excited energy level and the ground state.¹¹¹ For this model, the GKLS master equation [Eq. (13)] is a very good approximation for the energy population relaxation, provided the spectral density is not peaked.

The Harmonic bath is very popular and has been the inspiration for many approximations, for example, the influence functional approach allowing to integrate out the bath response.^{127,128}

A less restrictive use of the harmonic bath is to limit the growth of system-bath correlations employing the MultiConfiguration Time Dependent Hartree (MCDTH),^{129–132} for example, the study of the decay of an anharmonic oscillator into a bath of harmonic oscillators.¹³³ This method can take advantage of the semiclassical character of the harmonic modes and use Gaussian basis functions.¹³⁴ Since the growth of correlations is restricted, a multilayer bath is possible.¹³⁵

The problem with the Harmonic bath is that its ergodic properties are weak.¹³⁶ The linear coupling and the normal mode structure mean that the dynamics does not generate intermode entanglement. In addition, this bath has no internal mechanism that will lead to thermal equilibrium since each normal mode is independent.

One should point out that the noninteracting harmonic oscillator bath [Eq. (61)] does not fulfill the requirements of the eigenvalue thermalization hypothesis [Eq. (60)]. The bath ergodic properties are weak because it is a quasifree system with additional constants of motion.¹³⁶ This is the dilemma between employing solvable models and the reality of generic physical phenomena.

2. Spin bath

The spin bath is the other extreme model. The most general spin bath is the fully connected Hamiltonian

$$\hat{H}_B = \sum_j \omega_j \hat{\sigma}_z^j + \sum_{jklm} \mu_{lm}^{jk} \hat{\sigma}_l^j \cdot \hat{\sigma}_m^k, \quad (63)$$

where $\hat{\sigma}_l^j$, $l = x, y, z$ are the Pauli spin operators, ω_j are the spin frequencies, and μ_{lm}^{jk} is the connection tensor.¹³⁷ The Hamiltonian equation (63) is universal, meaning it can simulate any finite Hamiltonian. The system bath interaction to all spins becomes

$$\hat{H}_{SB} = \sum_{kj} g_K^j \hat{S}_k^j \otimes \hat{\sigma}_k^j, \quad (64)$$

where g_K^j are coupling parameters of the system to spin j .

A simplified spin flat bath imitates a normal mode bath [Eq. (61)],^{138–140}

$$\hat{H}_B = \sum_j \omega_j \hat{\sigma}_z^j. \quad (65)$$

Comparing this spin bath to the harmonic bath shows similarities and differences.^{133,141} For very small excitation and low temperature, both bath types converge. There is a mapping connecting the spectral density of the harmonic and the spin bath.¹⁴² The main difference in the system dynamics is that the spin bath is saturable, meaning that the amount of excitation each mode can absorb is limited. To overcome this difference, a spin bath can mimic a harmonic bath very closely by adding a spin transport term to the bath $\hat{H}_{B'} = \hat{H}_B + \sum_{jk} \kappa_{jk} (\hat{\sigma}_+^j \hat{\sigma}_-^k + \hat{\sigma}_-^j \hat{\sigma}_+^k)$. This term could be small. Nevertheless, it equilibrates the excess energy to all bath modes. Another important difference between bath models is the generation of large mode to mode entanglement in the spin bath which is absent in the harmonic bath.¹⁴¹ Thus, the ergodic properties of the spin bath are superior.

The finite spin bath is limited by recurrence. A well-studied model is a spin chain. The recurrence time in a spin chain is

determined by the speed of propagation of an event generated on the system bath interface.¹⁴³

More complex bath models have been studied^{144,145} which include extensive spin-spin coupling. Such models lead to thermalization according to the ETH hypothesis. The system-bath surrogate model cannot strictly reach equilibrium since the total dynamics is unitary $\hat{U} = e^{-\frac{i}{\hbar} \hat{H}t}$.

To test the ETH hypothesis, the dynamics of a small quantum system is coupled to a finite strongly coupled bath. In this case, we expect the system to converge to a canonical state. The operators of interest are local in the system. Therefore, according to the ETH, we expect them to relax to a value which is determined by the bath mean energy [Eq. (60)], with a correction to the finite heat capacity of the bath. This idea has been tested for a system consisting of one and two qubits and a bath consisting of 32 or 34 strongly and randomly coupled spins. The initial state of the bath was chosen as a random phase thermal wavefunction¹⁴⁶ [Eq. (75)]. A Hilbert size of $\sim 10^{11}$ employed for the study is in the limit of simulation by currently available classical computers. The ETH was verified with respect to the asymptotic system expectation values.^{137,147} In addition, for the one qubit case, a Bloch-type equation with time-dependent coefficients provides a simple and accurate description of the dynamics of a spin particle in contact with a thermal bath. A similar result was found for the 2-qubit system with a variety of bath models. Nevertheless, considering the eigenvalue thermalization hypothesis, the system dynamics will effectively equilibrate.¹³⁷ The effective bath size for a turnover to ETH has a Hilbert space dimension of $\sim 10^6$.

B. Stochastic thermal boundary

To overcome the problem of the unitary dynamics of the system and the primary bath, an additional secondary bath is introduced enforcing a GKLS boundary between the primary and the secondary bath (cf. Fig. 2),

$$\hat{H}_T = \hat{H}_S + \hat{H}_B + \hat{H}_{B''} + \hat{H}_{SB} + \hat{H}_{BB''}, \quad (66)$$

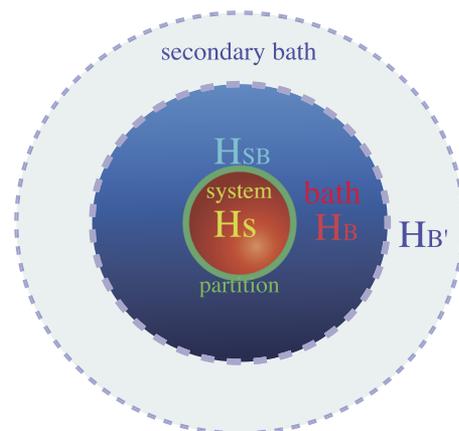


FIG. 2. System embedded in a primary bath. The GKLS boundary conditions connect the primary and the secondary bath meaning that $\hat{\rho} = \hat{\rho}_{SB} \otimes \hat{\rho}_{B'}$.



FIG. 3. A primary bath composed of six spins of different frequencies. The state of the individual spins is shown as a spot on the Bloch sphere. Spin 5 is swapped. This is a realization of a hard collision. A partial swap is also possible.

where $\hat{\mathbf{H}}_S$ represents the system, $\hat{\mathbf{H}}_B$ represents the primary bath, $\hat{\mathbf{H}}_{B''}$ represents the secondary bath, $\hat{\mathbf{H}}_{SB}$ represents the system-bath interaction, and $\hat{\mathbf{H}}_{BB''}$ represents the primary/secondary bath interaction.

For the secondary bath, the insights and structure of the repeated collision model (Sec. IV) will be used. It is natural to construct the secondary bath to be composed of noninteracting two-level-system (TLS) with the Hamiltonian

$$\hat{\mathbf{H}}_{B''} = \sum_j \omega_j \hat{\sigma}_z^j \quad (67)$$

and the state of the secondary bath

$$\hat{\rho}_{B''} = \hat{\rho}_1 \otimes \hat{\rho}_2 \cdots \otimes \hat{\rho}_j \cdots \quad (68)$$

and $\hat{\rho}_j = e^{-\beta \omega_j \hat{\sigma}_z^j} / Z$.

A possible choice for the case of a flat primary bath [Eq. (63)] is a secondary bath which is a clone of the primary bath (cf. Fig. 3).

The collision Markovian boundary conditions ensure that the system and primary bath will reach steady state. This steady state will become a correlated system-bath state. Is the reduced system state $\hat{\rho}_S$ the correct equilibrium state?

$$\hat{\rho}_S = \text{Tr}_B \left\{ \frac{1}{Z} e^{-\beta (\hat{\mathbf{H}}_S + \hat{\mathbf{H}}_B + \hat{\mathbf{H}}_{SB})} \right\}. \quad (69)$$

For this to happen, the primary-secondary bath interaction term should commute with the system bath Hamiltonian $[\hat{\mathbf{H}}_{BB''}, \hat{\mathbf{H}}_S + \hat{\mathbf{H}}_B + \hat{\mathbf{H}}_{SB}] = 0$. The simplest implementation is a local choice of $\hat{\mathbf{H}}_{BB''}$, for example, an interaction with the spins on the boundary of the primary bath. Such an interaction does not commute with the interaction term between the boundary spin and the rest of the primary bath, for example, $[\hat{\mathbf{H}}_{BB''}, \hat{\mathbf{H}}_{SB}] \neq 0$. Nevertheless, numerical tests showed consistency with thermodynamics. The heat flow through the system was from the hot to the cold bath.¹⁴⁸ In addition, the steady state of the system seems to correspond to Eq. (69).¹⁰¹

X. NUMERICAL IMPLEMENTATION

Quantum dynamical simulations are computationally demanding. Nevertheless, they are a necessary tool in supplying insight and guidance to experiment. In general, the computation cost scales exponentially with the number of degrees of freedom. To enable the computation, a careful allocation of the resources between the system and bath is required. In addition, parallel computation strategies have to be implemented. With typical calculations reaching a Hilbert

space size of 10^9 , the issue of accuracy becomes acute. The numerical procedures have to keep the accumulated errors below the accuracy determined by the computer representation.

A. State representation

The maximum size of Hilbert space is the limiting factor in the size of the quantum simulation. For example, 40 qubits have a Hilbert space size of $2^{40} \sim 10^{12}$ which is currently the limit of memory in high performance computing.

The natural description of an open quantum system employs a density operator $\hat{\rho}_{SB}$. An operator basis in Hilbert space is composed of $N \times N$ matrixes. This limits the direct calculation to the size of $2^{20} \sim 10^6$. This motivates the decomposition of the density operator to a sum of wavefunctions

$$\hat{\rho} \approx \frac{1}{M} \sum_k |\psi_k\rangle \langle \psi_k|, \quad (70)$$

where ψ_k is a specific realization typically stochastic. For stochastic sampling, the sum in Eq. (70) will converge to the state $\hat{\rho}$ as $\sim 1/\sqrt{M}$. For large complex quantum systems, this convergence can be very fast scaling with the size of Hilbert space as $\sim 1/\sqrt{N}$. This motivates the use of stochastic wavefunction methods to simulate large systems. An important example is the random phase thermal wavefunction Ψ_β .^{146,149–152} We first start with a random phase wavefunction composed of a superposition of all possible states of a complete basis with random phases

$$|\Phi(\vec{\Theta})\rangle = \frac{1}{\sqrt{N}} \sum_j e^{i\theta_j} |\phi_j\rangle, \quad (71)$$

where $|\phi\rangle$ is a complete basis and $\vec{\Theta} = \{\theta_1, \theta_2, \dots, \theta_j, \dots\}$ is a vector of random phases. The identity operator becomes

$$\hat{\mathbf{I}} = \lim_{K \rightarrow \infty} \frac{1}{K} \sum_k |\Phi(\vec{\Theta}_k)\rangle \langle \Phi(\vec{\Theta}_k)|, \quad (72)$$

where the average is over random realizations of $\vec{\Theta}$. The thermal state can be written as

$$\hat{\rho}_\beta = \frac{1}{Z} e^{-\frac{\beta}{2} \hat{\mathbf{H}}} \hat{\mathbf{I}} e^{-\frac{\beta}{2} \hat{\mathbf{H}}}. \quad (73)$$

Inserting Eq. (72) into Eq. (73) leads to

$$\hat{\rho}_\beta = \frac{1}{Z} \frac{1}{K} \sum_k |\Phi_\beta(\vec{\Theta}_k)\rangle \langle \Phi_\beta(\vec{\Theta}_k)|, \quad (74)$$

where the random phase thermal wavefunction is defined as

$$|\Phi_\beta(\vec{\Theta}_k)\rangle = e^{-\frac{\beta}{2} \hat{\mathbf{H}}} |\Phi(\vec{\Theta}_k)\rangle. \quad (75)$$

The convergence of this approximation is $O(\sqrt{K})$, where K is the number of realizations.¹⁴⁶ The stochastic thermal wavefunction can be obtained from the random phase wavefunction [Eq. (71)] by propagation in imaginary time $\beta/2$.¹⁵³ The choice of the functional basis determined the speed of convergence.¹⁵⁴

The memory allocation is the budget for the possible simulation. This budget is therefore distributed between the system and bath. For example, a 3-D system described by a grid of $N_S = 64^3 = 2^{24} \sim 4 \times 10^6$ points would leave only a Hilbert space size of $N_B = 2^{16} \sim 64 \times 10^3$ for the bath.

To enable large scale quantum simulation, the computation algorithm has to be economized. As a result, such calculations all rely on a sparse matrix vector basic operation

$$|\phi\rangle = \hat{\mathbf{H}}|\psi\rangle, \quad (76)$$

for wavefunction based methods, and

$$\hat{\sigma} = \mathcal{L}\hat{\rho} \quad (77)$$

for density operator calculations. These operations are vector matrix operations and, in general, scale as $O(N^2)$ for wavefunctions and $O(N^4)$ for density operators. Numerical techniques are focused on reducing this scaling to $O(N \log N)$ for wavefunctions and $O(N^2 \log N)$ for density operators. This scaling is found for the Fourier method^{155,156} as well as for spin dynamics.^{139,140}

B. Time propagation and other propagators

A dynamical simulation is typically performed either in the time domain or in the energy representation. In both cases, the actual implementation involves a function of an operator $f(\hat{\mathbf{H}})$. Considering the elementary step Eq. (76) or Eq. (77), a polynomial expansion of $f(\hat{\mathbf{H}})$ is advocated. Methods based on direct diagonalization scale as $O(N^3)$ for both computation effort and error accumulation. As a result, they become useless for large scale simulations.

A simulation in the time domain can be based on the time dependent Schrödinger equation

$$i\hbar \frac{d}{dt}\psi = \hat{\mathbf{H}}\psi \quad (78)$$

or the Liouville von Neumann equation

$$\frac{d}{dt}\rho = \mathcal{L}\rho. \quad (79)$$

Both equations have a common structure, in particular, when the Liouville space is vectorized. A polynomial approximation for the propagators become $\psi(t) \approx P_N(\hat{\mathbf{H}})\psi(0)$, where $P_N(\hat{\mathbf{O}})$ is a polynomial of order N in the operator $\hat{\mathbf{O}}$. The algorithm calculates the polynomial iteratively with the help of Eq. (76) or Eq. (77).

The polynomial chosen has to minimize the errors of the iterative procedure. For the time independent Hamiltonian, the Chebyshev polynomial expansion is optimal. Its main feature is that it does not accumulate errors even for polynomials of a very high degree, for example, 10^5 .¹⁵⁷ For the solution of the Schrödinger equation,

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar}\hat{\mathbf{H}}t}|\psi(0)\rangle = e^{-i\Phi} \sum_n a_n(t)|\phi_n\rangle, \quad (80)$$

where the global phase is $\Phi = (\Delta E/2 + E_{min})t$ and $a_n(t)$ are expansion coefficients $a_0(t) = J_0(\Delta Et/2)$ and $a_n = 2i^n J_n(\Delta Et/2)$, where ΔE is the

eigenvalue range of $\hat{\mathbf{H}}$ and J_n are Bessel functions. The vectors $|\phi_n\rangle = T_n(\hat{\mathbf{H}})|\psi(0)\rangle$ are evaluated by the Chebyshev recursion

$$|\phi_{n+1}\rangle = 2\hat{\mathbf{H}}|\phi_n\rangle - |\phi_{n-1}\rangle, \quad (81)$$

where \hat{H} is a normalized Hamiltonian with eigenvalues renormalized to $\{-1, 1\}$.^{157,158} A similar approach can be used for the Liouville von Neumann equation (79).¹⁵⁹

Chebyshev propagation in imaginary time has been developed to generate thermal wavefunctions [Eq. (75)] or the ground state.¹⁵³

Similar polynomial propagators have been developed for non-Hermitian \mathcal{L} ^{157,160–162} as well as for explicitly time dependent Hamiltonians.¹⁶³ An estimation of the minimum scaling of the computational effort for a quantum simulation is semilinear with the size of the Hilbert space and linear in the product of time and energy range. Polynomial propagators have superior accuracy to time stepping without sacrificing efficiency.

C. Stochastic wavefunction

There are infinitely many stochastic realizations of the open system dynamics. One can differentiate between linear and nonlinear implementations. Stochastic implementation of the GKLS equation was first developed employing a nonlinear implementation.^{103,164–166} Linear implementation is un-normalized and therefore unstable numerically. The nonlinear methods require a small time step.

Conversely, a linear numerical implementation of the stochastic surrogate Hamiltonian is performed. The system and primary bath are represented by a wavefunction $|\Psi_{SB}\rangle$ for each stochastic realization. The stochastic element is introduced by the collision model where the secondary bath is represented by a random thermal wavefunction of secondary spin j ,

$$|\psi_{B''}\rangle_j = \frac{1}{\sqrt{Z}} \left(e^{-\frac{1}{4}\beta\hbar\omega_j+i\theta}|+\rangle + e^{+\frac{1}{4}\beta\hbar\omega_j-i\theta}|-\rangle \right), \quad (82)$$

where ω_j is the frequency of spin j , θ is a random phase, and $Z = 2 \cosh(\frac{1}{2}\beta\hbar\omega_j)$.

The collision is represented by the unitary swap operation exchanging a spin between the primary and the secondary bath,¹⁴⁵

$$\hat{S}_{\omega} \psi_B \otimes \phi_{B''} = \phi_B \otimes \psi_{B''}. \quad (83)$$

The swapped spins are chosen at resonance. The swap unitary operation is the numerical tricky part of the implementation.¹⁴⁵ The swap rate Γ_j determines the rate of energy exchange between the primary and the secondary bath. A partial swap operation is also possible if $\hat{S} = e^{-\frac{i}{\hbar}\hat{V}\phi}$, then $\phi = \pi$ is a full swap but ϕ can be chosen to be small, leading to a partial swap.

Convergence of the model is obtained by increasing the number of bath modes and the number of stochastic realizations. As stated in Eq. (70), the convergence should scale as $O(\frac{1}{\sqrt{M}})$. However, the convergence also depends on the size of the primary bath. Empirically, it scales with the Hilbert space size of the primary bath as $O(\frac{1}{\sqrt{N}})$. As a result, very few realizations are required to converge a large stochastic simulation.^{146,154,167}

XI. SPECTROSCOPY AND CONTROL IN CONDENSED PHASES

The interaction of light with matter is one of the main venues to study the structure and dynamics of molecules. The wave nature of light allows carrying away the molecular information to a detector far field from the object. We can distinguish single photon encounters where both the light and the system have to be treated quantum mechanically. For stronger interacting fields, the radiation can be described semiclassically as a time dependent modulation of a molecular Hamiltonian.

A single photon theory is required for the quantum description of spontaneous emission. The multimode radiation field is then described as a harmonic bath. The primary molecular system is then coupled weakly to this bath. In this description, spontaneous emission can be viewed as heat dissipated into the radiation field bath. The WCL master equation then becomes the appropriate description of the system dynamics.

The strong field interactions are typically approximated as a time dependent driving field

$$\hat{H} = \hat{H}_M - \hat{\mu} \cdot \epsilon(t), \quad (84)$$

where \hat{H}_M is the molecular Hamiltonian, $\hat{\mu}$ is the dipole operator, and $\epsilon(t)$ the time dependent electromagnetic field. In the context of open quantum system, the energy current to the radiation field is classified as power $\mathcal{P} = \langle \frac{\partial \hat{H}}{\partial t} \rangle = -\langle \hat{\mu} \rangle \dot{\epsilon}$.⁷² This allows us to interpret absorption spectroscopy as the process of absorbing power from the radiation field and dissipating this power as heat to the environment. For a CW absorption model, both currents are balanced in a steady state. The spectrum becomes the dissipative power as a function of the driving frequency.¹ For a molecule in vacuum, the environment is the radiation field bath, and for molecules in the condensed phase, heat is dissipated to low frequency phonon modes. To be consistent with thermodynamics, the energy flow should always be from the external electromagnetic field to the bath.

Many spectroscopic descriptions do not adhere to this principle. For example, even the standard Bloch equation⁸⁴ can violate the II-law. The standard derivation of the WCL does not incorporate the external driving in the dissipative dynamics leading to a possible violation of the II-law.⁴⁰

Traditional spectroscopy is strongly biased toward a perturbative approach where the small parameter is the light-matter interaction.¹⁶⁸ These assumptions are in conflict with the current pulsed experimental techniques, where typically the peak intensity can be very high.

A comprehensive approach able to describe the full cycle of a pump-probe experiment is based on the surrogate Hamiltonian, for example, a direct time-domain spectroscopic computational model of a two pulse pump-probe approach. This scenario assumes a molecule at equilibrium perturbed by a first radiation pulse. The response after a time delay is interrogated by the second pulse. This generic scenario has been applied to cases of ultrashort and intense shaped pulses while the molecular system is embedded in the environment.

The steps in a pump-probe simulation¹⁴⁰ are as follows:

- the stationary initial state of the system and bath,
- the light induced excitation,

- the induced following dynamics,
- the interrogation by the second pulse,
- dissipation back to the original stationary state.

An example of a direct simulation of an ultrafast spectroscopic encounter in the time domain starts with a typical system Hamiltonian \hat{H}_S describing a ground electronic state and two coupled excited electronic states, a bright state coupled by a transition dipole and a dark state coupled nonadiabatically to the bright state,

$$\hat{H}_S = \begin{pmatrix} \hat{H}_g & -\hat{\mu}_{gb}\epsilon(t) & 0 \\ -\hat{\mu}_{bg}\epsilon^*(t) & \hat{H}_b & \hat{V}_{ba} \\ 0 & \hat{V}_{ab} & \hat{H}_a \end{pmatrix}, \quad (85)$$

and the molecular operators are functions of the nuclear coordinates:

$\hat{H}_k = \sum_j^N \frac{\hat{p}_j^2}{2m} + \hat{V}_k(\vec{r})$ is the surface Hamiltonian, and $\hat{V}_k(\vec{r})$ is the ground (g), bright (b), or acceptor (a) potential and all are function of the N nuclear coordinates \vec{r} . $\epsilon(t)$ represents the time dependent electromagnetic field. The instantaneous power absorbed from the pulse can be calculated using the first law [Eq. (54)]

$$\mathcal{P} = \left\langle \frac{\partial H}{\partial t} \right\rangle = 2\text{Real}(\langle \hat{\mu} \rangle \dot{\epsilon}). \quad (86)$$

The system-bath interaction \hat{H}_{SB} plays many roles in the spectroscopic encounter. The first is that it defines the initial state, i.e., the correlated system-bath state [Eq. (71)].^{140,146} This state is typically on the ground electronic state since the gap is large relative to the bath temperature.

During the excitation process, the relevant dissipation processes are electronic dephasing and vibrational dephasing and relaxation.^{101,140,144,169}

Specifically, for vibrational relaxation following excitation,¹⁰¹ the system-bath interaction becomes

$$\hat{H}_{SB} = f(\hat{\mathbf{R}}_s) \otimes \sum_j^N \lambda_j (\hat{\sigma}_j^\dagger + \hat{\sigma}_j), \quad (87)$$

where $f(\hat{\mathbf{R}}_s)$ is a dimensionless function of the system's coordinate $\hat{\mathbf{R}}_s$. λ_j is the system-bath coupling frequency of bath mode j . For a flat bath, the system-bath coupling is characterized by a spectral density $J(\omega)$ (units of frequency), then $\lambda_j = \sqrt{J(\omega_j)/\rho_j}$ and $\rho_j = (\omega_{j+1} - \omega_j)^{-1}$ is the density of bath modes.

The surrogate Hamiltonian method is well-matched to laser desorption.¹⁷⁰ Typically, the radiation field is strong and on the same timescale as the dissipation.

Spectroscopy simulations with the surrogate Hamiltonian is a prime choice when strong and fast pulses are applied. The method can be applied when the traditional methods based on perturbation theory fail. The surrogate Hamiltonian method can be applied for strong system bath interactions when there is no time scale separation between fast and slow dynamics.

A. Coherent control in open systems

Manipulating interfering pathways is the mechanism that leads to coherent control.^{171,172} Control is achieved through the use of time dependent external fields, and therefore, the system Hamiltonian is explicitly time dependent. Optimal Control Theory (OCT) is

the theoretical framework employed to obtain the control field. Initially, the control field is unknown. OCT obtains the control field by an iterative approach.^{173–175} This poses a challenge to OCT in open systems. The time dependent system Hamiltonian has to be incorporated in the dissipative dynamics, but the control field changes from iteration to iteration.

There are three common approaches to meet this challenge. The first is to ignore the influence of the time dependent field on the dissipative dynamics. This can be justified if the system bath interaction is very weak. The theoretical descriptions of OCT under these assumptions have been carried out in a density operator formalism using a static GKLS equation.^{176–181}

The second option is to incorporate the influence of the control field in the dissipative dynamics. A typical problem is acceleration of equilibration. A consistent time dependent GKLS equation is employed [Eq. (41)] in the density operator formalism. The equations of motion are modified using a reverse engineering approach.⁴⁸ Optimal control theory has also been incorporated using the hierarchical equations of motion (HEOM). For a spin Boson model, the time evolution of an open system density matrix strongly coupled to the bath has been solved. The populations of the two-level subsystem have been taken as control objectives. The optimal field consequently modifies the information back flow from the environment through different non-Markovian witnesses.¹⁸²

The third option is to employ the surrogate Hamiltonian approach where the control field is incorporated directly.^{183–185} The stochastic surrogate Hamiltonian method can serve as a consistent platform for quantum control in open systems. The main advantage is that the external driving is incorporated in a natural way without distorting the equations of motion. This feature has been incorporated in the study of weak field control.¹⁶⁹

A primary example of control in open systems is cooling the internal degrees of freedom of molecules. This means reduction of entropy of the systems. Directly the control field generates a unitary transformation which is entropy preserving. Only the interplay between the control field and the dissipation can lead to cooling.^{178,186,187} Cooling vibrational degrees of freedom in ultracold Cs₂ was demonstrated experimentally,¹⁸⁸ as well as cooling rotational degrees of freedom of AlH⁺.¹⁸⁹

Quantum control can be employed to counter the effects of dissipation. The idea is to apply a control field that will minimize the distance between the state of a system under dissipation and an isolated one.¹⁸¹ Analysis shows that this is equivalent to active cooling. Optimal control employing the surrogate Hamiltonian confirmed the analysis.^{183,184} Another open system example is performing a quantum gate under dissipative conditions.^{190,191}

For OCT, adding the environment has pros and cons.¹⁹² The drawback is that dissipation degrades coherence and thus degrades the interference. This forces a fast control protocol that can compete with the decoherence time scale. The positive side of adding an environment is that it increases the effective size of Hilbert space which can increase significantly the number of possible interference pathways.

XII. OVERVIEW

Practically, all quantum systems are open. The theory goes hand in hand with thermodynamics. Quantum mechanics and

thermodynamics are independent theories. Consistency between them when applied to a physical reality is a source of insight. This allows an independent check of a quantum computational model of an open system. A model which does adhere to thermodynamical laws is flawed. In this approach, the GKLS equation is the central pillar in the theory. It defines a quantum analog of an isothermal partition. In addition, it serves as a limiting case for more elaborate non-Markovian theories.

Simulating and modeling quantum open system encounters is the story of choosing the appropriate system-bath partition. The location of this partition has a profound influence on the success. For the description of a solvated small molecule, it is adequate to include in the system part the high frequency electronic and vibrational degrees of freedom and include in the bath the low frequency solvent modes. When the size of the molecule increases, the position of the partition is not clear cut. An example is the well-studied Fenna-Matthews-Olson (FMO) molecular complex composed of 7 to 8 chromophores.¹⁹³ This system has been modeled with almost all methods of quantum open systems.^{194–201} Initially, the system included only the excitonic manifold. This has been found inadequate due to vibrational degrees of freedom in resonance with the electronic degrees of freedom.^{128,202} Moving the system-bath boundary to include the vibrations is necessary but has a significant computational cost. The last word on a satisfactory FMO spectroscopic simulation is still in the future.¹⁷⁵

Due to the exponential scaling of computation resources with the number of quantum components, eventually only stochastic wavefunction methods will meet the challenge. We advocate the linear stochastic surrogate Hamiltonian method; nevertheless, other approaches may be more successful. In any case, consistency with the laws of thermodynamics is a strict criterion which all methods should meet.

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