Time Driven Quantum Master Equations and their Compatibility with the Fluctuation Dissipation Theorem

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We contribute to a long standing debate on the supposed failure of the Fluctuation Dissipation Theorem (FDT) for the Davies master equation (DME), an important class of Lindblad quantum master equations, describing time driven quantum systems weakly coupled to a heat bath. First we propose two simple and natural criteria on the driving which guarantees compatibility with the FDT. We show through our setting that, contrary to what often stated in the literature, the DME is fully compatible with the FDT. We thus argue that the cause of the dispute lies in the adopted perturbation scheme, rather than in the Lindblad character of the master equation itself. We confirm our statement by proving that the Grabert master equation, first proposed in [1] as an alternative linear dynamics fulfilling the FDT, is nothing else than the incriminated DME. Our criteria for the FDT can also be used in the analysis of the nonlinear thermodynamical master equation (NLTME), first obtained in the Brownian motion limit [2] and later independently rediscovered and generalized on thermodynamic grounds [3].

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I. INTRODUCTION

Quantum Markovian master equations [4–6] have shown to be of paramount importance in modeling decoherence and energy relaxation for open quantum systems for over 50 years [7–11]. Surely the most commonly found and adopted master equations are of linear type, in which case they are often required to have a Lindblad form for positivity requirements [6]. One of the reasons for this is that the Davies master equation (DME), is of Lindblad type, can be obtained as the weak coupling limit of a Hamiltonian model [12] and is also linked to the celebrated Fermi's Golden Rule [13, 14].

However, there has been much dispute around the physical consistency of a Lindblad dynamics for quantum dissipative master equations in the past [1, 2, 15–18] which is still ongoing at present [19–23]. In particular, focus was directed towards the linear response under a time driven external perturbation, where the Lindblad dynamics was argued to fail in providing the Fluctuation Dissipation Theorem (FDT) with Kubo canonical correlations [24, 25]. This led to rule out the Lindblad master equation as a physically acceptable dynamics. The claimed failure of the FDT led some authors to consider radically new alternative master equations [1, 2]. In particular, the weak coupling limit procedure was considerably revisited by Grabert in his book [1]. Therein (Chapter 5.4, Eq. (5.4.48)) Grabert claimed to have discovered a different linear master equation (GME), able to properly capture the physics of the weak coupling. The GME was argued *not* to be of the DME type and to be compatible with the FDT. Also, an important regime different from the weak coupling was explored: the Brownian motion regime [2]. This was shown to lead to yet another kind of master equation, acting nonlinearly on the density matrix. The nonlinear Grabert master equation was indeed originally proposed by Grabert in [2] and then independently rediscovered and further generalized with the nonlinear thermodynamic master equation (NLTME) in case of a nonequilibrium bath [3, 20]. As opposed to the DME, the latter equation was argued to be consistent with the FDT [2].

The claimed failure of the FDT for the DME is however at variance with a number of recent works (see e.g. [23, 26, 27]), and naturally demands to be clarified. This is the main motivation for the present work.

In this manuscript we study the linear response to a time driven perturbation of a quantum master equation, for a state initially at thermal equilibrium. We present two simple criteria on the perturbation, reported in Eq. (17) and in Eq. (19), which guarantee that the dynamics, possibly even nonlinear, is compatible with the FDT under Kubo structured correlations. We use those criteria to analyze the validity of the FDT theorem for the following three dynamics: DME, GME and NLTME. Our criteria for the perturbation are sufficient, but not necessary, to obtain the FDT, and model adiabatic drivings for dissipative quantum master equations.

Our main result is that the DME is indeed compatible with the FDT, and we argue that the claimed flaw of the DME lies in an inappropriate choice of the perturbation scheme, which only modifies the Hamiltonian part of the irreversible dynamics. To further confirm this, and this is our second result, we show that the GME coincides with the DME. This supports our main result, as Grabert himself in [1] was able to propose a perturbation scheme for the GME which is compatible with the FDT. More directly, we also offer a natural perturbation scheme for the DME which fulfills our criteria on the perturbation, thus proving the FDT for the DME. As a third result, we propose a natural perturbation scheme

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for the NLTME, which fulfills our criteria and thus guaranteed the FDT for the NLTME, in agreement to what was first proven by Grabert in [2]. This shows that our criteria on the perturbation schemes are able to account for potentially different physical regimes. Our fourth and last result is that the detailed balance properties of the GME [1] are directly transferred to the analogous notion [28, 29] for the DME. This is a corollary to our second result GME = DME, and suggests a new tool to potentially classify detailed balance quantum dynamical semigroups [30].

We point out that the perturbation scheme normally adopted does not meet our criteria, and only drives the reversible part of the master equation of interest while leaving the irreversible part untouched. Our schemes on the contrary affect the irreversible part as well as the reversible one. Concerning this, the FDT with Kubo canonical correlations is expected to hold true when the time modulation of the driving happens at the energy relaxation time scale [31]. This justifies our schemes as opposed to the normally adopted one, whose incompatibility with certain thermodynamic requirements has already been mentioned before (see e.g. [32] and references therein). We note however that if the driving oscillates faster, say on the reversible dynamics time scale, then a different FDT is expected to hold [33], with a different structure for the correlations than Kubo's [23], and perturbing the Hamiltonian part only could indeed make sense in that regime. In this work we only consider a driving varying on the energy relaxation time scale, as reflected in the strongly adiabatic character of the perturbation criteria which we propose and study.

We do not enter here in the merit of judging which of the two master equations surviving our analysis on the compatibility with the FDT (DME and NLTME) can best describe dissipative phenomena in quantum open system. In fact, these equations refer to different scaling limits in any case, and we postpone such analysis to a separate manuscript. We also remark that it is not our goal to use the criteria that we propose on the perturbation to classify all possible linear (or even worse nonlinear) master equations, on the basis of compatibility with the FDT. Indeed, on one side this is a challenging task beyond the scope of this work (see [34] to start with), and on the other side we don't claim that our criteria are necessary (which would be needed to start such a classification program): we just assert that they are sufficient.

We start by establishing the general framework and stating the FDT (Sec. II). In Section III we explain the main problematic point of the dispute that led several authors to rule out the Lindblad master equation as physically admissible. In Section IV we propose our natural criteria for a given perturbation scheme and show how they lead to the FDT. We then apply our simple scheme to the DME (Sec. V) and, after proving that the GME is the DME in Section VI, to the NLTME for a heat bath (Sec. VII A). Conclusions follow. A pictorial overview of the relations among the studied master equations can be found in Fig. 1. In this paper we take units such that $\hbar = 1$. Also, nowhere we consider Hamiltonian contribution coming from level renormalisation effects due to coupling with the bath: although such terms are numerically as relevant as are the dissipative terms, they pose no additional conceptual difficulty and, to our purposes here, only complicate notation and formulas. Also, we try to avoid all possible domain problems by always assuming to deal with finite dimensional Hilbert spaces for the systems of interest. In addition, we always assume suitable regularity properties of the time dependent driving force, in order to be able to manipulate the Born series.

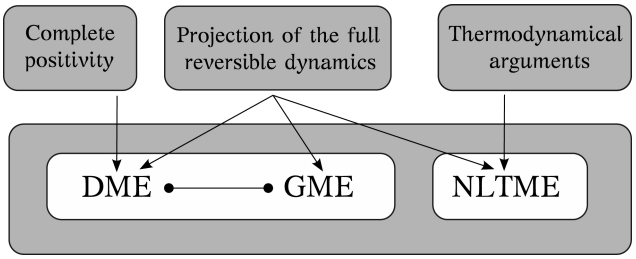

FIG. 1: Pictorial representation of the link between the different sets of examined master equations. Davies master equations (DME) are Lindblad equations often encountered in the weak coupling limit procedure and are defined in Eqs. (31, 35, 37). Grabert master equation (GME) is Eq. (5.4.48) of [1] (here reported in Eqs. (40, 41)) and it is a linear master equation argued therein to fulfill the FDT unlike the DME. The nonlinear thermodynamic master equation (NLTME) has been first found by Grabert as arising from the Brownian motion limit, and is here reported in Eq. (54), and then independently rediscovered and generalized out of equilibrium in [3].

II. GENERAL FRAMEWORK AND KUBO FDT

We introduce here the main objects that we deal with, and organize them in the framework of the FDT, as stated at the end of the section. We would like to stress here that our setting is that of the Callen-Welton-Kubo FDT [24, 35] for quantum systems in contact with a heat bath when the driving is caused by an external time-varying perturbation. This situation is quite different from Onsager's response; there the driving is generated by a difference of temperature or chemical potential between two or more reservoirs connected to the system [27].

We consider a quantum system S, described by the density matrix $\rho = \rho_t$ acting on the finite dimensional Hilbert space $\mathcal{H}_S$, and undergoing the dissipative evolution

$$\partial_t \rho = \mathcal{L}(\rho) \tag{1}$$

according to the time independent and *possibly nonlinear* dynamics $\mathcal{L}$. Given that the state manifold is $\mathcal{M} = \{\rho \,|\, \rho \geq 0,\ \mathrm{tr}(\rho) = 1\}$, the latter dynamics can

be seen as a map

$$\mathcal{L} : \mathcal{M} \longrightarrow T\mathcal{M} \tag{2}$$

from the state manifold to its tangent space $T\mathcal{M}$. We note that a typical fiber $T_\rho\mathcal{M}$ of $T\mathcal{M}$ at a state $\rho \in \mathcal{M}$ is isomorphic to the space $\mathrm{End}_{\mathrm{s.a.}}(\mathcal{H})$ of self-adjoint operators on $\mathcal{H}$. We suppose that the system at time is initially at equilibrium with respect to a given Hamiltonian H_S, in the Gibbs state

$$\pi := \frac{e^{-\beta H_S}}{\mathrm{tr}(e^{-\beta H_S})} \tag{3}$$

relative to an inverse temperature $\beta = (k_B T)^{-1}$, so that in particular

$$\mathcal{L}(\pi) = 0. \tag{4}$$

We emphasize that we do not make the hypothesis here that $\mathcal{L}$ is a Lindblad operator, and actually we do not even assume that $\mathcal{L}$ is linear. What we do require is that, as a map on the state manifold $\mathcal{M}$, the dynamics $\mathcal{L}$ admits a tangent map $T\mathcal{L} : T\mathcal{M} \to T\mathcal{M}$ and that π is also a steady state

$$\bar{\mathcal{L}}\pi = 0 \tag{5}$$

for the tangent map $\bar{\mathcal{L}} := T_\pi\mathcal{L}$ at the equilibrium state π. The tangent map $T_{\bar\rho}\mathcal{L}$ of a map $\mathcal{L} : \mathcal{M} \to T\mathcal{M}$ at $\bar\rho \in \mathcal{M}$ can be defined through the embedding $\mathcal{M} \subset \mathrm{End}_{\mathrm{s.a.}}(\mathcal{H})$ as the (unique, when it exists) linear map for which

$$\lim_{\rho\to\bar\rho} \frac{\mathcal{L}(\rho) - \mathcal{L}(\bar\rho) - T_{\bar\rho}\mathcal{L}\,(\rho - \bar\rho)}{\|\rho - \bar\rho\|} = 0 \tag{6}$$

in the induced topology on $\mathcal{M}$ (more colloquially, the element ρ in the above formula should approach $\bar\rho$ within $\mathcal{M}$, so that $\mathcal{L}(\rho)$ can make sense). In particular, it follows from Eq.s (4, 5) that if $\mathcal{L}$ is linear, then $\bar{\mathcal{L}} = \mathcal{L}$. Note that we do not ask that the linear map $\bar{\mathcal{L}}$ be of Lindblad type. We only suppose that the true dynamics $\mathcal{L}$ preserves positivity for physical reasons, but not even this requirement is relevant to our present analysis, and we do not require that $\bar{\mathcal{L}}$ preserves positivity. At time $t = 0$ we turn on a weak time dependent driving of the Hamiltonian part of the dynamics according to

$$H_S \longrightarrow (H_S)^\epsilon_t := H_S + \epsilon E(t) v, \tag{7}$$

where v is a Hermitian operator, $E(t)$ is a real function modeling the driving in time and ϵ is a small real parameter. We suppose that, as a consequence,

$$\mathcal{L} \longrightarrow \mathcal{L}^\epsilon_t \tag{8}$$

where the dependence upon the driving is yet unspecified, although we do suppose it to be regular in ϵ and t, and that the perturbed density matrix ρ^ϵ_t undergoes the perturbed dynamics

$$\partial_t \rho^\epsilon_t = \mathcal{L}^\epsilon_t(\rho^\epsilon_t). \tag{9}$$

Let the observable u be measured at time $t > 0$: its expectation value is $\langle u\rangle_{\rho^\epsilon_t} := \mathrm{tr}(u\rho^\epsilon_t)$, which is presumed to have an expansion in ϵ of the causal form

$$\mathrm{tr}(u\rho^\epsilon_t) = \mathrm{tr}(u\pi) + \epsilon \int_0^t E(t-s)\chi_{uv}(s)\, ds + o(\epsilon). \tag{10}$$

We say that the dynamics in Eq. (1) together with the perturbation scheme in Eq. (9) fulfills the FDT if the implied *linear susceptibility* $\chi_{uv}(t)$ has the specific form

$$\chi_{uv}(t) = \beta\, \partial_t \langle u(t)\,;\, v\rangle_\beta \tag{11}$$

where $u(t) = e^{\bar{\mathcal{L}}^* t} u$ is u evolved at time t through the dual $\bar{\mathcal{L}}^*$ of $\bar{\mathcal{L}}$ [43], and the *Kubo canonical correlations*

$$\langle a\,;\, b\rangle_\beta := \mathrm{tr}(aK_\pi b) \tag{12}$$

are defined through the linear superoperator K_ρ for a general density matrix ρ through

$$K_\rho b := \int_0^1 \rho^\lambda b \rho^{1-\lambda} d\lambda. \tag{13}$$

The meaning of the FDT in Eq. (11) is that the linear response to an applied time driven perturbation is entirely determined by the fluctuations of the unperturbed system around equilibrium. We note that our definition of the FDT coincides with and generalizes the usual one related to $\mathcal{L}$ being linear. When $\mathcal{L}$ is a genuine nonlinear dynamics, our definition of the system fluctuations should be regarded as the best guess for the Heisenberg evolution $e^{\bar{\mathcal{L}}^* t}$ around equilibrium, when the system deviations from equilibrium feel the linear dynamics $\bar{\mathcal{L}} = d\mathcal{L}(\pi)$. Obviously this is a generalization, because in the linear case $\bar{\mathcal{L}} = \mathcal{L}$ recovers the standard definition (see e.g. [2]). We will need such a generalization to be able to speak of FDT for the NLTME later on.

III. PROBLEM WITH THE COMMON PERTURBATION SCHEME

We now present a widely encountered situation [32, 36–39] where the FDT fails to be met. Consider a quantum system under the above setting, whose governing dynamics $\mathcal{L}$ is of Lindblad type (and so $\mathcal{L} = \bar{\mathcal{L}}$) and of the form

$$\mathcal{L}\rho = \delta_{H_S}\rho + \mathcal{K}\rho \tag{14}$$

where $\delta_{H_S}\rho := -i[H_S, \rho]$ is the standard Liouville superoperator relative to a system Hamiltonian H_S and $\mathcal{K}$ is a dissipative linear dynamics which, and this is the crucial fact, is assumed *not* to depend on H_S. Adding the time dependent perturbation $\epsilon E(t)v$ to the Hamiltonian H_S as in Eq. (7) gives Eq. (9) with

$$\mathcal{L}^\epsilon_t \rho^\epsilon_t = -i[H_S + \epsilon E(t) v, \rho^\epsilon_t] + \mathcal{K}\rho^\epsilon_t. \tag{15}$$

Then one can prove (see Appendix A) that

$$\begin{aligned}\chi_{uv}(t) &= -i\mathrm{tr}(ue^{\mathcal{L}t}[v,\pi]) = \beta\mathrm{tr}(ue^{\mathcal{L}t}(-i[H_S,K_\pi v])) \\ &= \beta\mathrm{tr}(ue^{\mathcal{L}t}(\mathcal{L}-\mathcal{K})K_\pi v) \\ &= \beta\,\partial_t\langle u(t)\,;\,v\rangle_\beta - \beta\langle(\mathcal{K}^*u(t))\,;\,v\rangle_\beta \qquad (16)\end{aligned}$$

where as usual we have indicated with a * the Heisenberg dual. The first line of the above expression for the susceptibility is exactly what Grabert obtained in [2] by perturbing the linear dynamics Eq.(14) in the linear response regime at equilibrium. Together with the second line above, this clearly shows the departure from the FDT unless $\mathcal{K}=0$ and the system is purely reversible.

This highly problematic situation led Grabert [2] to conclude that the Lindblad dynamics commonly employed for quantum open systems, which indeed has the form (14), was incompatible with the FDT and hence not physically admissible.

Quite contrary to Grabert's conclusions, we show thereafter that the true cause of the failure of the FDT does not lie in the Lindblad dynamics itself, but rather in an incorrect implementation of the perturbation scheme (8) in Eq. (15). There in fact, only the reversible part of the dynamics gets perturbed by the driving, and the irreversible part is left untouched. What we find to be wrong about Eq. (15) is the statement that the dissipative part $\mathcal{K}$ of the dynamics does not depend on the Hamiltonian H_S, and is therefore left unmodified by the driving. That the driving affects the dissipative part of the dynamics too is an important message, which will be encoded into general criteria to correctly account for the driving, as we shall now see.

Before doing that, we would just like to comment on the reason why the problem of the failure of the FDT, conceptually crucial for quite some researchers, has temporarily been swept under the carpet by many others: if $\mathcal{K}$ is the dissipative part of the Lindblad operator in Eq.(35), then the ratio $\frac{\|\mathcal{K}\|}{\|\delta_{H_S}\|}$ of the dissipative over the reversible part is generally small (as e.g. in a weak coupling regime). So, the deviation from the proper Kubo structure of the susceptibility in Eq.(16) is numerically negligible (typically for confined quantum systems, where the two norms are finite). However master equations almost always found their usefulness in regimes in which the coupling is small but finite. Thus, making sure that the FDT is obtained at an exact level is surely desirable, both conceptually and in applications.

IV. TWO NATURAL CRITERIA FOR THE PERTURBATION SCHEME

We present here two natural criteria for the perturbation scheme of the given (possibly nonlinear) dissipative dynamics, able to guarantee the compatibility with the FDT in Eq. (11). The two criteria are rather minimal and natural, they coincide in case the dynamics is linear and will later on be shown to be met both by the DME (=GME) and by the NLTME. They are reported in Eq. (17) and in Eq. (19).

We suppose that the perturbed (and possibly nonlinear) dynamics $\mathcal{L}_t^\epsilon$ depends on the driving in such a way as to fulfill

$$\mathcal{L}_t^\epsilon(\pi_t^\epsilon) = 0 \qquad (17)$$

with respect to the *accompanying density matrix*

$$\pi_t^\epsilon := \frac{e^{-\beta(H_S)_t^\epsilon}}{\mathrm{tr}\left(e^{-\beta(H_S)_t^\epsilon}\right)} \qquad (18)$$

which represents the Gibbs time-local equilibrium with respect to the current time Hamiltonian $(H_S)_t^\epsilon$. Naming with $\bar{\mathcal{L}}_t^\epsilon = T_{\pi_t^\epsilon}\mathcal{L}_t^\epsilon$ the tangent map of $\mathcal{L}_t^\epsilon$ at π_t^ϵ, we now assume that

$$\bar{\mathcal{L}}_t^\epsilon \pi_t^\epsilon = 0 \qquad (19)$$

(as in the unperturbed case), so that π_t^ϵ is a zero of the tangent map $\bar{\mathcal{L}}_t^\epsilon$ too. Hence for all density matrices ρ

$$\mathcal{L}_t^\epsilon(\rho) = \bar{\mathcal{L}}_t^\epsilon\rho + o(\|\rho-\pi_t^\epsilon\|), \qquad (20)$$

see Eq. (6) and thereafter for the notation. The meaning of the criteria in Eq. (17) and in Eq. (19) is straightforward: the perturbation is adiabatic, and the quasi-steady state properties of the linearized dynamics are compatible with the adiabatic perturbation (i.e. the accompanying density matrix is in the kernel of the linearized dynamics at each time step).

Note that if $\mathcal{L}_t^\epsilon$ is linear, then $\bar{\mathcal{L}}_t^\epsilon = \mathcal{L}_t^\epsilon$. We are now going to show that under the above natural and simple conditions (17) and (19), which are central to us, the perturbation scheme $\mathcal{L} \longrightarrow \mathcal{L}_t^\epsilon$ fulfills the FDT according to our definition in Eq. (11). Let ρ_t^ϵ be the solution to Eq. (9): to proceed, first we note that Eq. (20) and the expansion $\rho_t^\epsilon = \pi_t^\epsilon + \epsilon\,\delta\rho + O(\epsilon^2)$ give

$$\mathcal{L}_t^\epsilon(\rho_t^\epsilon) = \bar{\mathcal{L}}_t^\epsilon\,\rho_t^\epsilon + o(\epsilon). \qquad (21)$$

Let us call W_t^ϵ the evolution operator of the linear perturbed dynamics $\bar{\mathcal{L}}_t^\epsilon$ in (9) from the initial time $t=0$ to current time t, so that

$$W_t^\epsilon = \mathcal{T}\exp\left(\int_0^t \bar{\mathcal{L}}_{t'}^\epsilon\,dt'\right), \qquad (22)$$

where $\mathcal{T}$ indicates the time ordering, and denote with $W_t = \exp\left(\bar{\mathcal{L}}t\right)$ the evolution operator associated to the unperturbed linear dynamics $\bar{\mathcal{L}}$. Then Eq.s (21, 22) implies that

$$\rho_t^\epsilon = W_t^\epsilon\pi + o(\epsilon) \qquad (23)$$

Now we compute

$$\begin{aligned}W_t^\epsilon - W_t &= (W_{t-s}W_s^\epsilon)|_{s=0}^{s=t} \\ &= \int_0^t \partial_s(W_{t-s}W_s^\epsilon)\,ds \\ &= \int_0^t W_{t-s}(\bar{\mathcal{L}}_s^\epsilon - \bar{\mathcal{L}})W_s^\epsilon\,ds \\ &= \epsilon\int_0^t W_{t-s}\,\bar{\mathcal{L}}_s'\,W_s\,ds + o(\epsilon), \qquad (24)\end{aligned}$$

where we expanded the time-dependent linear generator $\bar{\mathcal{L}}_t^\epsilon$ to the first order in ϵ, that is

$$\bar{\mathcal{L}}_t^\epsilon = \bar{\mathcal{L}} + \epsilon\,(\partial_\epsilon \bar{\mathcal{L}}_t^\epsilon)|_{\epsilon=0} + o(\epsilon), \tag{25}$$

and denoted $\bar{\mathcal{L}}_t^{'} := (\partial_\epsilon \bar{\mathcal{L}}_t^\epsilon)|_{\epsilon=0}$. Applying Eq.s (23, 24, 25) to $\langle u\rangle_{\rho_t^\epsilon} = \mathrm{tr}(u\rho_t^\epsilon) = \mathrm{tr}(uW_t^\epsilon\pi) + o(\epsilon)$ gives

$$\langle u\rangle_{\rho_t^\epsilon} = \langle u\rangle_\pi + \epsilon \int_0^t \mathrm{tr}(uW_{t-s}\,\bar{\mathcal{L}}_s^{'}\,\pi)\,ds + o(\epsilon). \tag{26}$$

noting that $\mathrm{tr}(uW_t\pi) = \mathrm{tr}(u\pi) = \langle u\rangle_\pi$. Now, starting from our central Eq. (19) and taking its derivative with respect to ϵ at $\epsilon = 0$ yields $\bar{\mathcal{L}}_s^{'}\,\pi = -\bar{\mathcal{L}}\,\pi_s^{'}$, where again we used the notation $\pi_s^{'} = (\partial_\epsilon \pi_s^\epsilon)|_{\epsilon=0}$. One also computes explicitly for the deformation in Eq. (7) that

$$\begin{aligned}\pi_s^{'} &= \lim_{\epsilon\to 0}\frac{1}{\epsilon}(\pi_s^\epsilon - \pi)\\ &= -\beta E(s) K_\pi v - (\partial_\epsilon \ln \mathrm{tr}(e^{-\beta(H_S)_s^\epsilon}))|_{\epsilon=0}\,\pi,\end{aligned} \tag{27}$$

where we have utilized the Duhamel's formula

$$e^A - e^B = \int_0^1 e^{\lambda A}(A-B)e^{(1-\lambda)B}d\lambda. \tag{28}$$

Substituting these results in Eq. (26) gives

$$\langle u\rangle_{\rho_t^\epsilon} = \langle u\rangle_\pi + \epsilon\beta \int_0^t E(s)\mathrm{tr}(ue^{\bar{\mathcal{L}}(t-s)}\,\bar{\mathcal{L}}\,K_\pi v)\,ds + o(\epsilon), \tag{29}$$

and changing the time integration variable according to $s \mapsto t - s$ then yields Eq. (10) with the susceptibility

$$\chi_{uv}(t) = \beta\,\mathrm{tr}(ue^{\bar{\mathcal{L}}t}\,\bar{\mathcal{L}}K_\pi v), \tag{30}$$

which through duality is equivalent to Eq. (11) using the definition of the Kubo canonical correlations. This shows that the above perturbation scheme, guaranteeing an accompanying density matrix π_t^ϵ of the Gibbs form in Eq. (18), is able to ensure the FDT with the proper Kubo structure in the linear response regime. In the sequel, we apply this scheme to the master equations we are interested in, namely the DME and the NLTME, to show that both satisfy the required assumptions and thus are compatible with the FDT.

V. APPLICATION TO THE DAVIES MASTER EQUATION

In this section we consider the DME, an important class of Lindblad master equations, often found as a weak coupling limit dynamics of an underlying Hamiltonian evolution for the system of interest coupled to a heat bath. We propose a perturbation scheme to the DME and show the compatibility with the FDT.

A. Definition of the DME

We want here to define what we mean by DME [8, 12]. It is given in terms of the Davies generator $\mathcal{D}$ through

$$\partial_t\rho \;=\; \mathcal{D}\rho = \mathcal{D}(H_S, Q, \hat{h})\rho. \tag{31}$$

Its functional dependence on the system and bath degrees of freedom is made explicit here. Namely, the Davies generator $\mathcal{D}$ depends on the system Hamiltonian H_S and on a Hermitian coupling operator Q, both acting on the system's Hilbert space $\mathcal{H}_S$ and implementing the system reversible and irreversible couplings respectively. The bath influence on the system comes then from the *spectral function* $\hat{h}$ [12]. By the latter we mean any positive real function with the detailed balance property [28, 29]

$$\hat{h}(\nu) = e^{\beta\nu}\hat{h}(-\nu), \tag{32}$$

which relates emission and absorption rates through the proper Boltzmann factor. To further specify the DME, it is convenient to introduce the so called *eigenoperators* A_ν related to a given system pair (H_S, Q). Their matrix elements with respect to the Hamiltonian H_S basis $\{|n\rangle\}$ are

$$(A_\nu)_{n,n'} = Q_{n,n'}\,\delta_{E_n - E_{n'},-\nu} \tag{33}$$

where δ is the Kroenecker delta and $H_S|n\rangle = E_n|n\rangle$, for the energy E_n of the level $|n\rangle$. The A_ν's are called eigenoperators because they fulfill the eigenvector equation

$$\delta_{H_S}A_\nu = i\nu A_\nu \tag{34}$$

relative to the reversible Liouvillian $\delta_{H_S} := -i[H_S, \cdot]$ (introduced in Section III). Note that $A_\nu = 0$ if $\nu \notin \mathrm{sp}(\delta_{H_S})$ is not in the spectrum of δ_{H_S}. Then with the above ingredients and notations, the DME is characterised by the following structure

$$\begin{aligned}\mathcal{D}\rho \;&:=\; \delta_{H_S}\rho\\ &+\;\frac{1}{2}\sum_{\nu\in\mathrm{sp}(\delta_{H_S})}\hat{h}(\nu)\,([A_\nu\rho, A_{-\nu}] + [A_\nu, \rho A_{-\nu}])\end{aligned} \tag{35}$$

It is important to remark that properties reported in Eq.s (34, 32) imply the detailed balance conditions [28–30] with respect to the Gibbs state π given in Eq. (3), which is the unique steady state under natural ergodic conditions on the eigenoperators A_ν (like that the identity is the only operator commuting with H_S and all the A_ν's) or equivalently on the coupling operator Q.

We remark that whenever desired, the functional dependence in Eq. (35) can be interpreted in terms of the eigenoperators $A_\nu = A_{-\nu}^\dagger$ according to $\mathcal{D}(H_S, \{A_\nu(Q, H_S)\}_\nu, \hat{h}) = \mathcal{D}(H_S, \{A_\nu\}_\nu, \hat{h})$, by putting

$$Q = \sum_{\nu\in\mathrm{sp}(\delta_{H_S})} A_\nu. \tag{36}$$

For further use we finally note that, as for all the master equations we deal with in this paper, the definition of the DME can easily be extended to multiple Hermitian couplings Q_α, in which case a positive *spectral matrix* $\hat{h}_{\alpha\alpha'}(\nu)$ should be introduced [12, 28, 40] with the detailed balance property $\hat{h}_{\alpha\alpha'}(\nu) = e^{\beta\nu}\hat{h}_{\alpha'\alpha}(-\nu)$ and

$$\begin{aligned}\mathcal{D}\rho \;&:=\; \delta_{H_S}\rho \qquad (37)\\ &+\; \frac{1}{2}\sum_{\substack{\alpha,\,\alpha'\\ \nu\,\in\,\mathrm{sp}(\delta_{H_S})}} \hat{h}_{\alpha,\alpha'}(\nu)\left([A_{\alpha',\nu}\rho, A_{\alpha,-\nu}] + [A_{\alpha',\nu}, \rho A_{\alpha,-\nu}]\right)\end{aligned}$$

where $A_{\alpha,\nu}$ would again be defined from Q_α by Eq. (33).

B. Spectral matrix from the weak coupling limit

The weak coupling limit procedure (see e.g. [8, 11, 12]) gives a prescription for the the spectral matrix $\hat{h}$ entering Eq. (37) in terms of a bath correlation function. The starting point is a system S coupled to a bath through a Hamiltonian coupling: then, the limit dynamics is obtained by studying the system S at large times and for weak coupling. In this case, the heat bath is described by a Gibbs state $\sigma := \frac{e^{-\beta H_B}}{\mathrm{tr}\, e^{-\beta H_B}}$ relative to a bath Hamiltonian H_B and to an inverse temperature β, and the coupling between the system and the bath is taken to be $H' = \sum_\alpha Q_\alpha \otimes \Phi_\alpha$, for some bath coupling operators Φ_α. Then, with the variation $\delta\Phi_\alpha := \Phi_\alpha - \mathrm{tr}(\sigma\Phi_\alpha)$ and with $\delta\Phi_\alpha(t) := e^{iH_B t}\delta\Phi_\alpha e^{-iH_B t}$, one obtains precisely Eq. (37) with spectral matrix

$$\hat{h}_{\alpha,\alpha'}(\nu) = \int_{-\infty}^{\infty} e^{i\nu t}\mathrm{tr}(\sigma\,\delta\Phi_\alpha(t)\,\delta\Phi_{\alpha'})\,dt. \qquad (38)$$

It can be shown that such $\hat{h}_{\alpha,\alpha'}(\nu)$ obeys the detailed balance condition $\hat{h}_{\alpha,\alpha'}(\nu) = e^{\beta\nu}\hat{h}_{\alpha',\alpha}(-\nu)$ and is a positive matrix [11, 12, 40].

C. FDT for the DME

We are now in position to present a simple perturbation scheme able to ensure the FDT for the Davies master equation. Indeed from the functional relation Eq. (31) and from Eq. (35) we see that the dissipative part of the Davies master equation depends explicitly not only on the coupling operator but also on the system Hamiltonian. This is just enough to guarantee that the steady state is the Gibbs state relative to H_S. A Davies generator $\mathcal{D}(H, Q)$ written in terms of a Hamiltonian H has as a steady state the Gibbs state relative to H.

Thus, we immediately deduce that the conditions in Section IV of our approach, which in the linear case boil down to Eq. (19), can be easily satisfied by establishing the following perturbation scheme $\mathcal{D} \longrightarrow \mathcal{D}_t^\epsilon$:

$$\left\{\begin{array}{rcl} H_S & \longrightarrow & (H_S)_t^\epsilon \\ \mathcal{D} & \longrightarrow & \mathcal{D}_t^\epsilon := \mathcal{D}((H_S)_t^\epsilon, Q, \hat{h}). \end{array}\right. \qquad (39)$$

Above, $(H_S)_t^\epsilon$ is specified by Eq. (7), and the perturbed Davies generator can be written more explicitly through Eq. (33) by substituting $\delta_{H_S} \longrightarrow \delta_{(H_S)_t^\epsilon}$ and $A_\nu \longrightarrow (A_\nu)_t^\epsilon := A_\nu(Q, (H_S)_t^\epsilon)$ in Eq. (35). The scheme in Eq. (39) is just enough to guarantee that the Gibbs state π_t^ϵ in Eq. (18) is indeed the accompanying density matrix $\mathcal{D}_t^\epsilon\pi_t^\epsilon = 0$ for the perturbed Davies generator $\mathcal{D}_t^\epsilon$. Inspired by the statistical mechanics interpretation of the spectral function given in Sec. V B, we do not modify $\hat{h}$, because we assume that the bath dynamics stays unperturbed, while the system alone is subject to the external driving.

This proves that the FDT in Eq. (11) for Davies master equations holds true, contrary to what is found in the literature (see Section III). What has been crucial to solve the puzzle of the FDT for the Davies master equation was the observation that *the linear generator depends on the driving both in its reversible and irreversible parts.*

We observe that the coupling operator Q need neither depend on the temperature nor on the system Hamiltonian H_S. However, it could. In this case, it could be natural to perturb the coupling operator too. The resulting new perturbation scheme $\mathcal{D} \longrightarrow \mathcal{D}_t^\epsilon := \mathcal{D}((H_S)_t^\epsilon, Q_t^\epsilon, \hat{h})$ would still guarantee Eq. (19) and thus the FDT. This shows that *the perturbation scheme need not be unique.*

Our perturbation scheme in Eq. (39) is related to what was discussed in [31] in a more formal, but yet different setting, where the authors write the susceptibility $\chi_{uv}(t)$ for a time driven underlying Hamiltonian system taken in the weak coupling limit. Contrary to our case, the limit susceptibility in [31] does not fulfill the FDT exactly (only if u and v commute with H_S it does). However, our susceptibility in Eq. (11) for the DME case $\bar{\mathcal{L}} = \mathcal{D}$ and the one in [31] agree in the weak coupling limit.

VI. GRABERT MASTER EQUATION

The apparent failure of the FDT for the Lindblad dynamics suggested by the arguments of section III has brought a number of authors to look for physically sound alternatives. One of the main features on which the weak coupling procedure applied to quantum open systems relies is the assumption of an initially factorized state of system+bath. Grabert and coworkers were among the first to suggest that this could have been an exceedingly severe restriction to using the Lindblad dynamics [1, 2, 15, 16, 19]. In particular Grabert proposed another master equation (GME) in his book [1], that he showed to guarantee the FDT. Namely, it is proven in the book [2] (Chapter 5) how *(i)* the GME is deduced starting from the idea, thermodynamical in flavor, that the initial state is non-factorized, and is rather described in terms of a nonzero chemical potential operator deforming the equilibrium Gibbs state of the global Hamiltonian of system+reservoir (including the interaction Hamiltonian H'); *(ii)* the linear response of such linear master equation is perfectly compatible with the detailed balance and

FDT (Eq. (5.5.12) and Eq. (6.5.23) respectively in the book [2]).

In order to contribute to the debate on the thermodynamical consistency of the linear quantum dynamics for dissipative systems, we state here (the technical part of the proof is reported in Appendix B) that the GME is actually nothing else than a (very interesting) reformulation of the DME in Eq. (37). This result not only enforces the compatibility of the DME furnished in Eq. (37) with the FDT, but also shows that the perturbation scheme need not be unique, as far as the FDT is concerned. We would also like to mention at this point that, surprising as this might appear a priori, the result that the GME is the same as the DME despite the fact that the initial state is different can be understood a posteriori with the help of the following argument: for a quantum system of interest that is confined in space, the initial system+bath correlations are local and bounded, and proportional to the coupling H'. As one takes the weak coupling limit (as also Grabert does), such correlations are washed away and cannot be seen at large times (see e.g. Section 3.1.1 in [41] and Section 4.6.9 in [42]).

A. GME and DME: two sides of the same coin

Now, concerning the GME in Eq. (5.4.48) of [1], we recast it here in our notation. First of all, a system Hamiltonian H_S is given, together with the same setting of Section V B. In Eq. (5.4.36) of [1] Grabert takes the most general interaction Hamiltonian $H' = \sum_\alpha Q_\alpha \otimes \Phi_\alpha$ coupling the system to the bath through system coupling operators Q_α and bath coupling operators Φ_α. Then Grabert writes H' using the eigenoperators $A_{\alpha,\nu}$ which spectrally decompose Q_α as they are defined in Eq. (33). From $Q_\alpha = \sum_\nu A_{\alpha,\nu}$ we obtain Eq. (5.4.36) in the form $H' = \sum_{\alpha,\nu} A_{\alpha,\nu} \otimes \Phi_\alpha$, with the eigenoperators fulfilling Eq. (34). Then, neglecting the reversible renormalisation terms as we have also done for the Lindblad dynamics (but they could be taken into account as well, at the expenses of a slightly longer calculation) the Grabert linear master equation reads

$$\partial_t \rho = \mathcal{G}\rho = \mathcal{G}(H_S, \{Q_\alpha\}, \{\Phi_\alpha\})\rho \tag{40}$$

for the following Grabert generator $\mathcal{G}$:

$$\mathcal{G}\rho = \delta_{H_S}\rho - \frac{1}{2}\sum_{\substack{\alpha,\,\alpha' \\ \nu \,\in\, \mathrm{sp}(\delta_{H_S})}} [A_{\alpha,-\nu}, (\widetilde{K}^{\nu}_{\alpha\alpha'})_\pi [A_{\alpha',\nu}, (K_\pi)^{-1}\rho]]. \tag{41}$$

Here the tilded superoperator $(\widetilde{K}^{-\nu}_{\alpha\alpha'})_\pi$ is defined as

$$(\widetilde{K}^{\nu}_{\alpha\alpha'})_\pi X = \int_{-\infty}^{\infty} dt\, e^{i\nu t} \int_0^1 d\lambda\, \mathrm{tr}(\sigma\, \delta\Phi_\alpha(t)\, \sigma^\lambda \delta\Phi_{\alpha'} \sigma^{-\lambda})\, \pi^\lambda X \pi^{1-\lambda} \tag{42}$$

where σ is the Gibbs state of the bath. The superoperator K_π has instead already been defined in Eq. (13) for $\rho = \pi$. To write Grabert master equation Eq. (5.4.48) of Grabert's book [1] in this form, we have used Eq. (5.4.37, 5.4.43, 5.4.50) therein.

Now in the Appendix B we prove the important result that

$$\mathcal{G} = \mathcal{G}(H_S, \{Q_\alpha\}, \{\Phi_\alpha\}) = \mathcal{D}(H_S, \{Q_\alpha\}, \hat{h}_{\alpha,\alpha'}) = \mathcal{D} \tag{43}$$

for the Davies generator $\mathcal{D}$ reported in Eq. (37) with precisely the same spectral matrix $\hat{h}_{\alpha\alpha'}(\nu)$ appearing in Eq. (38). This not only shows that the Grabert linear master equation is of Lindblad (and actually Davies) form: it also shows that the Grabert linear master equation is precisely the very Davies master equation which is obtained in the weak coupling limit procedure starting from the same Hamiltonian ingredients.

Since Grabert in [1] furnishes a proof of the FDT for his master equation, while mistakenly claiming the failure of the FDT for the Davies master equation, this means once again that the problem with the FDT cannot be the Davies master equation, but rather the choice of the perturbation scheme.

B. A new notion of Detailed Balance for the DME

Although Grabert's master equation does not offer an alternative to the DME, as we have seen, it contributes in shining light on the thermodynamic structure of the DME itself, at the level of the detailed balance notion and of the FDT, as we now argue. The detailed balance property appearing in Eq. (5.5.12) in the book [1] applied to a linear generator $\mathcal{L}$ reads

$$\mathcal{L}^* = \Theta K_\pi^{-1} \mathcal{L} K_\pi \Theta\,, \tag{44}$$

where Θ is a time inversion superoperator. This is a similar, but different and interesting, alternative to the usual detailed balance condition [16, 28]

$$\mathcal{L}^* = \Theta L(\pi)^{-1} \mathcal{L} L(\pi) \Theta\,, \tag{45}$$

where $L(\rho)X := \rho X$ is the multiplication from the left, and to the so called standard detailed balance condition [30]

$$\mathcal{L}^* = \Theta (L(\pi^{1/2})R(\pi^{1/2}))^{-1} \mathcal{L} (L(\pi^{1/2})R(\pi^{1/2})) \Theta\,, \tag{46}$$

where $R(\rho)X := X\rho$ is the multiplication from the right. In fact, we find that the microscopic detailed balance condition in Eq. (32) implies all of the identities above for the Davies generator (as well as the analogous identity for the multiplication from the right). To better see the connection among the definitions above, note that $K_\pi = \int_0^1 Y_\lambda(\pi)\, d\lambda$ with $Y_\lambda(\pi) = L(\pi^\lambda)R(\pi^{1-\lambda})$, and $Y_1(\pi) = L(\pi)$ and $Y_{1/2}(\pi) = L(\pi^{1/2})R(\pi^{1/2})$. Grabert's detailed balance condition just seems more symmetrical than the one normally employed, and we find that it is a better restatement of the concept that both the reversible and the irreversible dynamics commute with the

modular group $e^{it\ln\pi}$ associated to the steady state π of the dynamics itself [29]. Moreover, Grabert's detailed balance condition is associated to the Kubo canonical scalar product $\langle A\,;\,B\rangle := \int_0^1 \mathrm{tr}(\pi\, A\, e^{\lambda\ln\pi}\, B\, e^{-\lambda\ln\pi})\, d\lambda$, and better respects the positivity properties when passing to the dual description through this scalar product. This fact could potentially offer a new perspective on the classification of detailed balance Quantum Dynamical Semigroups [30].

C. Grabert's perturbation scheme

Concerning the FDT, Grabert's analysis offers an alternative approach to compute the linear response of the DME. Indeed, by defining a chemical potential operator μ that describes the deviation of the state ρ from the equilibrium π through

$$\rho = \rho_\mu = \frac{e^{-\beta(H_S-\mu)}}{Z}, \tag{47}$$

Grabert argues that the perturbation Eq. (7) should simply translate in

$$\mu \longrightarrow \mu + \epsilon E(t) v, \tag{48}$$

which in turns leads to the following prescription for the DME (see Eq. (6.5.22) in [1])

$$\mathcal{G} \longrightarrow \mathcal{G}_t^\epsilon \rho := \mathcal{G}(\rho + \epsilon\beta E(t) K_\pi v) + o(\epsilon) \tag{49}$$

valid to first order in ϵ and for a slowly varying (i.e. adiabatic) field $E(t)$. We see here how Grabert prescription to include the perturbation also touches the dissipative part of the dynamics, unlike the common and mistaken prescription described in Section III: once again this confirms that what is really relevant for the DME to be compatible with the FDT is a correct prescription for the perturbation. Now, the solution to $\mathcal{G}_t^\epsilon$ is

$$\rho_t^\epsilon = e^{\mathcal{G}t}\rho_0 + \epsilon\beta \int_0^t E(t-s) e^{\mathcal{G}s}\mathcal{G}K_\pi v\, ds + o(\epsilon). \tag{50}$$

When traced this expression against an observable u, and using $\rho_0 = \pi$ as initial condition, it immediately gives the FDT in Eq. (11) for the linear susceptibility.

We remark that Grabert prescription, when seen through the concept of chemical potential operator shift in Eq. (48) looks more thermodynamical in flavor than our prescription. However we will see in the next section how closely related the two perturbation schemes are, by applying our scheme to the NLTME for a bath at equilibrium. For the moment, we limit ourselves to observe that the scheme we have presented here does not fulfill the criteria (17) and (19). In fact, we stress once more that those criteria are only sufficient, and not necessary, to prove the FDT.

D. An alternative perturbation scheme

In the effort to make the connection between the DME and the GME, we prove in Appendix B that the DME can be cast in the form of (B2) reported here below

$$\partial_t\rho = \delta_{H_S}\rho - \frac{1}{2}\sum_{\substack{\alpha,\,\alpha' \\ \nu\,\in\,\mathrm{sp}(\delta_{H_S})}} \hat{h}_{\alpha\alpha'}(\nu)[A_{\alpha,-\nu}, K_\pi^{-\nu}[A_{\alpha',\nu}, (K_\pi)^{-1}\rho]], \tag{51}$$

where we have introduced the frequency dependent superoperator K_ρ^ν through

$$K_\rho^\nu X = \int_0^1 e^{\lambda\beta\nu}\rho^\lambda X \rho^{1-\lambda}\, d\lambda \tag{52}$$

for any observable X (note that $K_\rho^0 = K_\rho$). Inspired by such form, we now consider the following perturbation

$$\begin{aligned}\partial_t\rho \;=\; & \delta_{(H_S)_t^\epsilon}\rho \\ & -\frac{1}{2}\sum_{\substack{\alpha,\,\alpha' \\ \nu\,\in\,\mathrm{sp}(\delta_{H_S})}} \hat{h}_{\alpha\alpha'}(\nu)[A_{\alpha,-\nu}, K_{\pi_t^\epsilon}^{-\nu}[A_{\alpha',\nu}, (K_{\pi_t^\epsilon})^{-1}\rho]].\end{aligned} \tag{53}$$

As we will see, this establishes a formal analogy to the perturbation scheme of the NLTME (see e.g. Eq. (62)), where the operators explicitly appearing inside the double commutator (no matter if coupling operators or eigenoperators) are not perturbed. The above perturbation scheme fulfills criterion (17) (criterion (19) is automatically fulfilled because of linearity) and thus guarantees the FDT with susceptibility (11). This is a simple consequence of $(K_{\pi_t^\epsilon})^{-1}\pi_t^\epsilon = 1$. However, since the eigenoperators are not changed by the perturbation, we can conclude that the scheme in Eq. (53) is different from (and alternative to) the scheme in Eq. (39). Without reference to the microscopic origins of the perturbation (i.e. an underlying Hamiltonian model) discriminating between the two schemes is not possible if only the linear response is considered: Only the response at orders higher than linear could then indicate what the appropriate choice could be.

VII. APPLICATION TO THE NONLINEAR THERMODYNAMIC MASTER EQUATION

A. Brownian Motion Limit and the Nonlinear Thermodynamic Master Equation

Motivated by shortcomings of the linear response of the Lindblad dynamics, which as we have shown are only apparent, Grabert has proposed a novel, nonlinear master equation (NLGME) for the density matrix [2], later on independently found as a particular case of the NLTME for a heat bath at equilibrium [3, 20]. We observe that in [2, 15] the nonlinear dissipative equation is claimed to describe a regime different from the weak coupling,

called *Brownian Motion Limit*, which is the *slow motion* limit of the system variables relative to the bath variables. A typical example, as reported in [2] is that of a massive Brownian particle scattering with many light bath particles. This procedure is different from the weak coupling limit, which explains why the resulting equation has a different nature with respect to the DME. While postponing to a separate work the study of the precise relation between the weak coupling and the Brownian regime as meant in [2, 15], we argue here that the bath variables are assumed to be fast in the sense that they relax very quickly to equilibrium after colliding with the system (i.e. the collision time is very small, to allow for a Markovian prescription). Then, the slow motion of the system is intended with the idea that out of a single collision the system only receives an infinitesimal amount of energy, and many collisions are needed to see a finite, yet quantum, effect.

Instead, the NLTME has been proposed based on geometric and thermodynamic grounds, like the positivity of the entropy production and Kubo brackets [20]. Nevertheless, the fact that it corresponds to the nonlinear Grabert master equation for an equilibrium bath seems to suggest that the NLTME could also arise as a scaling limit of an underlying Hamiltonian dynamics. We leave such conjectures to future analysis, as said, and we use in the sequel the reference to the NLTME by understanding the bath to be at equilibrium.

Even if Grabert already proved the compatibility of the NLTME with the FDT in [2], we would like here to apply our perturbation scheme, to see how close it is to Grabert's approach, the latter being based on the idea of parametrizing the response density matrix through a chemical potential operator as in Eq. (47). The NLTME

$$\partial_t \rho = \mathcal{J}(\rho) \tag{54}$$

is defined by the vector field $\mathcal{J} = \mathcal{J}(H_S, Q)$ through

$$\mathcal{J}(\rho) := \delta_{H_S}\rho - \frac{\gamma}{\beta}[Q, K_\rho[Q, \ln\rho + \beta H_S]], \tag{55}$$

and it is written relative to a Hermitian coupling operator Q that generates the dissipative term, to the system Hamiltonian H_S and to a positive *friction* term γ. Note that the nonlinearity appears through the presence of K_ρ, defined in Eq. (13). Generalization to many coupling operators results in

$$\mathcal{J}(\rho) := \delta_{H_S}\rho - \sum_{\alpha,\alpha'} \frac{\gamma_{\alpha,\alpha'}}{\beta}[Q_\alpha, K_\rho[Q_{\alpha'}, \ln\rho + \beta H_S]] \tag{56}$$

for a positive friction matrix $\gamma_{\alpha,\alpha'}$, and only complicates notation for our purposes here, which is why we will only consider Eq. (55) in the sequel.

B. FDT for the NLTME

Discussing the perturbation scheme in Eq. (54) is actually straightforward, thanks to the explicit appearance of the Hamiltonian H_S in the dissipative part. It is then sufficient to take

$$\begin{cases} H_S \longrightarrow (H_S)^\epsilon_t \\ \mathcal{J} \longrightarrow \mathcal{J}^\epsilon_t := \mathcal{J}((H_S)^\epsilon_t, Q). \end{cases} \tag{57}$$

Now let $\bar{\mathcal{J}}^\epsilon_t := T_{\pi^\epsilon_t}\mathcal{J}^\epsilon_t$ be the tangent map of $\mathcal{J}^\epsilon_t$ at the accompanying density matrix π^ϵ_t. The FDT follows if the two main conditions Eq. (17) and Eq. (19) are fulfilled. We first check the analogous conditions for the unperturbed case, namely Eq. (4) and Eq. (5), and then observe that the former conditions are completely analogous. This is so because the ϵ dependence is only given through the perturbed Hamiltonian $H_S \longrightarrow (H_S)^\epsilon_t$, and the steady state of $\mathcal{J}(H, Q)$ is always the Gibbs state relative to H, no matter what H is (just as for the Davies master equation).

First, seeing that the Gibbs state π of the system is the steady state of the vector field $\mathcal{J}$ is immediate because $\beta H_S = -\ln\pi + c$ for a c-number. This fulfills Eq. (4). As for the linear generator $\bar{\mathcal{J}} = d\mathcal{J}(\pi)$ we will show in a moment that

$$\bar{\mathcal{J}}\rho := \delta_{H_S}\rho - \frac{\gamma}{\beta}[Q, K_\pi[Q, K^{-1}_\pi\rho]]. \tag{58}$$

Concerning the condition in Eq. (5) for $\bar{\mathcal{J}}$, it follows from $K_\pi 1 = \pi$ that $K^{-1}_\pi\pi = 1$ and so $\bar{\mathcal{J}}\pi = 0$. As for the conditions in Eq. (17) and in Eq. (19), it is straightforward to realize that $\mathcal{J}^\epsilon_t\pi^\epsilon_t = 0$ (as $\beta(H_S)^\epsilon_t = -\ln\pi^\epsilon_t + c$) and it will be immediate from the lines below that Eq. (19) follows as well. With this, we are in condition to apply our scheme of Section IV: this ensures the FDT for the NLTME.

The importance of the generator $\bar{\mathcal{J}}$ with respect to the FDT was first recognized by Grabert in [2]. Its derivation can be understood in a simple way, which we report here because of its thermodynamic flavor. Following Grabert, every density matrix can be parametrized as in Eq. (47) by a chemical potential operator μ. Using Eq. (28) we have

$$\rho_\mu - \pi = \beta\int_0^1 \rho^\lambda_\mu \mu \pi^{1-\lambda}\, d\lambda = \beta K_\pi\mu + o(\|\mu\|) \tag{59}$$

It follows that

$$\ln\rho - \ln\pi = \beta\mu = K^{-1}_\pi(\rho - \pi) + o(\|\rho - \pi\|). \tag{60}$$

Plugging this into $\mathcal{J}(\rho)$ in Eq. (54), evaluating all the rest (namely K_ρ) at π and realizing that $\mathcal{J}(\pi) = 0$ and $K^{-1}_\pi\pi = 1$ gives precisely

$$\mathcal{J}(\rho) = \bar{\mathcal{J}}\rho + o(\|\rho - \pi\|) \tag{61}$$

with the tangent map $\bar{\mathcal{J}} = T_\pi\mathcal{J}$ given in Eq. (58). It is evident that the above can all be retold for $\pi \longrightarrow \pi^\epsilon_t$ by declaring the chemical potential operator to be defined with respect to the perturbed $(H_S)^\epsilon_t$. This gives $\bar{\mathcal{J}}^\epsilon_t$ through

$$\bar{\mathcal{J}}^\epsilon_t\rho = \delta_{(H_S)^\epsilon_t}\rho - \frac{\gamma}{\beta}[Q, K_{\pi^\epsilon_t}[Q, K^{-1}_{\pi^\epsilon_t}\rho]] \tag{62}$$

and proves Eq. (19).

VIII. CONCLUSIONS

We have contributed to a long standing debate on the compatibility of certain Markovian quantum master equation (DME) with the FDT for fluctuations of Kubo type in connection with the linear response to an external driving. In particular, we have shown that the DME is fully compatible with the FDT, contrary to what is sometimes claimed in the literature. We find that what is usually suspected as a flaw of the DME is actually a flaw of the perturbation scheme normally adopted, which perturbs only the Hamiltonian part of the dynamics, and leaves the dissipative part untouched. We have argued that this procedure is not consistent for adiabatic drivings. We have proposed two simple criteria which can be used to test a general quantum master equation (possibly nonlinear) on its thermodynamic admissibility with respect to the FDT. The criteria conform to the idea of an adiabatic perturbation, and implement the requirement that the adiabatic states should at all times be the equilibrium states of the driving (Eq. (17) and Eq. (19)). We then proposed natural perturbation schemes for the DME which meet those criteria, and thus show compatibility of the DME with the FDT. We have also shown that the alternative GME is just a reformulation of the DME. This is important because the GME was originally proposed as an alternative candidate master equation, which should substitute the DME in the description of the weak coupling limit, on the basis that the GME would fulfill the FDT contrary to the DME. Once again this shows that the DME is not problematic, unlike the applied perturbation scheme, which may be. Our criteria also apply to nonlinear master equations: as an application, we have proposed a natural and compatible perturbation scheme for the NLTME, thus confirming the FDT for the latter, in agreement with what is already shown in [2]. We have discussed the non unicity of the perturbation scheme: noting that DME = GME, three different schemes were suggested for the DME, in Eq.s (39, 49, 53) respectively, which give the same linear response. Further restrictions could be obtained by considering the response at higher orders. Finally, using the GME reformulation of the DME unravels some thermodynamic aspects of the DME. For instance, it directly leads to a definition, new to the authors' knowledge, of the detailed balance property for quantum dynamical semigroups, which the DME fulfills. As an outlook, guided also by the thermodynamic perspective of the GME over the DME, which seems to reveal a structure similar to that of the NLTME, we hope in the near future to be able to address the important question of the validity regimes of the DME versus the NLTME.

Appendix A: Common problem with FDT

Let us call W_t^ϵ the evolution operator of the perturbed dynamics $\mathcal{L}_t^\epsilon$ in (9) from time 0 to time t and denote with $W_t = e^{\mathcal{L}t}$ the evolution operator associated to the unperturbed dynamics $\mathcal{L}$. Then Eq. (24) and Eq. (26) apply, where $\mathcal{L}'_t := (\partial_\epsilon \mathcal{L}_t^\epsilon)|_{\epsilon=0}$ can be directly computed to be

$$\mathcal{L}'_t \rho = -iE(t)[v,\rho]. \tag{A1}$$

Plugging this into Eq. (26) and using the property $[v,\pi] = \beta[H_S, K_\pi v]$ gives Eq. (16). It remains to show that this property holds. Naming $\pi_\alpha := \frac{e^{-\beta(H_S-\alpha v)}}{\mathrm{tr} e^{-\beta(H_S-\alpha v)}}$, expanding

$$\pi_\alpha - \pi = \alpha\beta K_\pi\, v + o(\alpha) \tag{A2}$$

and then taking the commutator with H_S gives

$$[H_S, \pi_\alpha] = \alpha\beta [H_S, K_\pi\, v] + o(\alpha). \tag{A3}$$

The wanted property follows by adding and subtracting $[-\alpha v, \pi_\alpha]$ to the l.h.s., noting that $[H_S - \alpha v, \pi_\alpha] = 0$, dividing by α and evaluating at $\alpha = 0$.

Appendix B: GME is DME

The Fourier transform in Eq. (42) can actually be carried on, by noting that $\mathrm{tr}(\sigma\, \delta\Phi_\alpha(t)\, \sigma^\lambda \delta\Phi_{\alpha'} \sigma^{-\lambda}) = \mathrm{tr}(\sigma\, \delta\Phi_\alpha(t - i\beta\lambda)\, \delta\Phi_{\alpha'})$ and using the analyticity properties of the KMS state σ, this gives

$$\begin{aligned}(\widetilde{K}^\nu_{\alpha\alpha'})_\pi X &= \int_{-\infty}^{\infty} e^{i\nu t}\, \mathrm{tr}(\sigma\, \delta\Phi_\alpha(t)\, \delta\Phi_{\alpha'})\, dt \\ &\quad \times \int_0^1 e^{-\lambda\beta\nu} \pi^\lambda X \pi^{1-\lambda}\, d\lambda \\ &= \hat{h}_{\alpha\alpha'}(\nu)\, K_\pi^{-\nu} X \end{aligned} \tag{B1}$$

where $K_\pi^{-\nu}$ is defined by Eq. (52) and $\hat{h}_{\alpha\alpha'}$ is the bath spectral matrix in Eq. (38). Putting the results together casts the Grabert master equation Eq. (5.4.48) of [1] in the form

$$\partial_t \rho = \delta_{H_S}\rho - \frac{1}{2} \sum_{\substack{\alpha,\,\alpha' \\ \nu\,\in\,\mathrm{sp}(\delta_{H_S})}} \hat{h}_{\alpha\alpha'}(\nu) [A_{\alpha,-\nu}, K_\pi^{-\nu}[A_{\alpha',\nu}, (K_\pi)^{-1}\rho]]. \tag{B2}$$

For sake of completeness we add that this master equation differs from Eq. (5.4.48) of [1] only for a reversible term (a Hamiltonian renormalisation), which however we always neglect in the present work (also for the Lindblad dynamics), and surely is out of the debate concerning the FDT and the thermodynamical admissibility. We now prove that Eq. (B2) can be cast in Lindblad form, and is actually nothing else than the Davies master equation.

First, from the fact that all eigenoperators $A_{\alpha,\nu}$ fulfill Eq. (34), one deduces that

$$e^{-\lambda\beta H_S} A_{\alpha,\nu} = e^{\lambda\beta\nu} A_{\alpha,\nu} e^{-\lambda\beta H_S}. \tag{B3}$$

With this, one can prove that

$$K_\pi^\nu [A_{\alpha,-\nu}, X] = A_{\alpha,-\nu} K_\pi(X) - e^{\beta\nu} K_\pi(X) A_{\alpha,-\nu} \tag{B4}$$

where X is any operator. We also note that the positive spectral matrix $\hat{h}_{\alpha\alpha'}$ has the important detailed balance property $\hat{h}_{\alpha\alpha'}(\nu) = e^{\beta\nu}\hat{h}_{\alpha'\alpha}(-\nu)$ (see e.g. [28, 40]). With this, and inserting Eq. (B4) into Eq. (B2) one obtains

$$\begin{aligned}
\partial_t\rho &= \delta_{H_S}\rho - \frac{1}{2}\sum_{\nu,\alpha,\alpha'}\hat{h}_{\alpha\alpha'}(\nu)[A_{\alpha,-\nu},(A_{\alpha',\nu}\rho - e^{-\beta\nu}\rho A_{\alpha',\nu})] \\
&= \delta_{H_S}\rho + \frac{1}{2}\sum_{\nu,\alpha,\alpha'}\hat{h}_{\alpha\alpha'}(\nu)[A_{\alpha',\nu}\rho, A_{\alpha,-\nu}] + \frac{1}{2}\sum_{\nu,\alpha,\alpha'}\hat{h}_{\alpha'\alpha}(-\nu)[A_{\alpha,-\nu},\rho A_{\alpha',\nu}] \\
&= \delta_{H_S}\rho + \frac{1}{2}\sum_{\nu,\alpha,\alpha'}\hat{h}_{\alpha\alpha'}(\nu)([A_{\alpha',\nu}\rho, A_{\alpha,-\nu}] + [A_{\alpha',\nu},\rho A_{\alpha,-\nu}]),
\end{aligned} \tag{B5}$$

which is precisely the Davies master equation Eq. (37) for the very same spectral matrix in Eq. (38) originating via the standard weak coupling limit procedure.

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