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Fluctuations and entanglement in open quantum systems

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Chapter 1.

Introduction

The subject of this thesis is the study of the class of the *Open Quantum Systems*, i.e. quantum systems which are in weak interaction with an external environment, often acting as a reservoir, and whose evolution is consequently influenced by this interaction.

Since the coupling of the system with the reservoir is weak, it makes sense to try to disentangle the dynamics of the system of interest from the global time-evolution. However, a particular attention must be taken in the derivation of the reduced evolution law, which is expressed by a *Master Equation*. When the *reduced dynamics* of the system has to be extracted from the dynamics of the compound system, different Master Equations can be obtained by the application of different kinds of Markovian approximations, which in turn give different evolution laws.

In order to sort out the disparate often incompatible open quantum dynamics, a leading criterion is to ensure that they do not violate important physical properties that a proper reduced dynamics must fulfill. In primis the positivity requirement, that ensures that any physical initial state is mapped into another physical state at any later time. Secondly, the complete positivity condition, that guarantees that physical consistency is preserved also when dealing with open quantum systems which are entangled with other systems. Usually, complete positivity is justified in terms of the existence of entangled states of the open quantum system coupled to an arbitrary, inert ancilla. Complete positivity avoids the appearance of negative probabilities in the spectrum of the time-evolving states of system plus ancilla. The main bulk of this thesis work is to show that a non completely positive dynamics can lead to violations of the Second Law of Thermodynamics.

The thesis is structured in the following way.

After a short introduction to Open Quantum System theory, the properties of *positivity* and *complete positivity* are presented and their importance is explained. Then, a few types of Master Equations are briefly summarized and their differences are stressed. In the third chapter we discuss the Second Law of Thermodynamics in the context of the open quantum systems and we put in evidence the connection between complete positivity and the Second Law. In the fourth chapter a specific open quantum system is examined, constituted by a minimal three-sites circuit whose current is produced by a single free electron. The circuit is immersed in a dissipative thermal bath and driven by an alternating potential. Its evolution with time and in particular the asymptotic stsates are studied, with respect to two different Master Equations. We show – through analytical and numerical means – that only when the Master Equation is derived, in the *weak coupling limit*, in according to the so-called Davies's prescription of eliminating the fast oscillations via an ergodic average, the requirements of complete positivity are fulfilled and the Second Law of Thermodynamics is not violated, while more rough approximations may give rise to negative entropy production.

In the last chapter we focus on the possible metrological applications of entanglement, and in particular on the possibility of improving the estimation of quantum parameters by preparing systems of many ultra-cold atoms in entangled states. After introducing a suitable notion of entanglement which takes into account the indistinguishability of identical particles, we show that *spin-squeezing* techniques are not useful to improve the sensitivities of interferometric measurements when dealing with systems of identical bosons.

Chapter 2.

Open Quantum Systems

The primary subject of study in Quantum Mechanics is the class of closed quantum systems, namely those systems that can be considered isolated. The time-evolution of a closed quantum system is described by means of a one-parameter group of unitary operators on a Hilbert space mapping the initial state onto its evoluted at a given time t. The group structure ensures that the dynamics is completely reversible: this means that the knowledge of the physical state at time t allows to determine the physical state at any time t', that can be taken to be in the future or in the past of t.

Nevertheless many real-world physical systems are not isolated, as they interact in a non-negligible way with the surrounding systems, what we call the *environment*. The latter is generally viewed as a much larger system, consisting of a very high number of degrees of freedom (possibly infinite). When dealing with an open quantum system one cannot assume that its dynamics is reversible, because the interaction with the environment, which involves exchange of energy and entropy, provokes the breaking of the reversibility. Of course if one decides to study the environment E and the open system S as a whole, then the total system $S+E$ is again a closed system; but its dynamics can be practically impossible to determine. Due to the extreme complication in the description of a system with infinite degrees of freedom one might try to single out the evolution of the system S, which is the relevant one.

The idea underlying the study of the open quantum systems, instead, is to examine those situations in which the interaction between the system S and the environment E is weak enough to allow the description of S and its dynamics by referring to its own degrees of freedom. By means of suitable approximations which lead to a *Master Equation*, the reduced dynamics of the system is determined with sufficient precision and embodies dissipation and noisy effects caused by the interaction system-environment.

The literature on Open Quantum Systems is very large. In the references we have listed only a selection of the relevant publications [1–16], without the claim to be exhaustive.

In Quantum Mechanics a physical system is described introducing a Hilbert space whose normalized vectors represent its possible states. In the case of small systems with a finite number n of degrees of freedom – the case in which we are mainly interested – this Hilbert space can be identified with $\mathbb{C}^n$. Furthermore, a subclass of the set of linear operators on $\mathbb{C}^n$, the Hermitian operators, corresponds to the set of the physical observables of the system. They can be represented by the algebra $M_n(\mathbb{C})$ of $n \times n$ complex Hermitian matrices $X = X^\dagger$.

The dynamics of a closed quantum system is determined by a Hermitian operator $H \in M_n(\mathbb{C})$, the Hamiltonian, entering the expression of the Schrödinger equation

$$\partial_t \left|\psi_t\right\rangle = -iH \left|\psi_t\right\rangle, \quad (\hbar \equiv 1).$$

The statistical character of standard Quantum Mechanics is based on the idea of considering, instead of a single physical system, a large collection of identical systems $\mathcal{E} = \{S^{(1)}, S^{(2)}, \ldots, S^{(N)}\}$ that can be prepared in the same experimental conditions, defined by some suitable parameters. This *ensemble* is described at time t by a normalized vector $|\psi_t\rangle$ in the Hilbert space of states $\mathbb{C}^n$, as mentioned above.

A second postulate fixes the statistical interpretation (due to Von Neumann [17]): the measurable quantities are represented by self-adjoint operators on $\mathbb{C}^n$, called *observables*; the outcomes of the process of measurement of an observable R are exactly the real values r of its spectrum; this spectrum is characterized by a distribution function $f_\psi(r)$ that allows to determine the probability that the outcome falls into a given subset $B \subset \mathbb{R}$:

$$P(B) = \int_B r f_\psi(r) \mathrm{d}r$$

and the expectation value

$$E(R) = \langle R \rangle_\psi = \int_{-\infty}^{+\infty} r f_\psi(r) \mathrm{d}r = \langle \psi \,|\, R \,|\, \psi \rangle .$$

2.1. Density matrix formalism

A more general way to represent quantum statistical ensemble of S is the *density matrix formalism.* It consists in considering a collection of M ensembles $\mathcal{E}_1, \mathcal{E}_2, \ldots, \mathcal{E}_M$, each described by a normalized vector $|\psi_\alpha\rangle$, $\alpha = 1, \ldots, M$ in $\mathbb{C}^n$. Taking a large number N_α of systems from each $\mathcal{E}_\alpha$ we obtain a new ensemble $\mathcal{E}$ of $N = \sum_\alpha N_\alpha$ systems. We call *weights* the ratios $w_\alpha = N_\alpha / N$. It follows that the mean value of the observable R is now given by the expression

$$E(R) = \sum_\alpha w_\alpha \langle \psi_\alpha \,|\, R \,|\, \psi_\alpha \rangle .$$

Introducing the *density matrix*

$$\rho = \sum_\alpha w_\alpha \left|\psi_\alpha\right\rangle \left\langle\psi_\alpha\right| , \tag{2.1}$$

the *expection value* can be computed as a *trace operation*:

$$E(R) = \mathrm{T}r(R\rho) \equiv \sum_i \langle \phi_i \,|\, R\rho \,|\, \phi_i \rangle \,,$$

for an arbitrary orthonormal basis $\{|\phi_i\rangle\}_{i=1,\ldots,n} \subset \mathbb{C}^n$.

Since $0 \leq w_\alpha \leq 1$, $\sum_\alpha w_\alpha = 1$, from (2.1) it easily verified that ρ is self-adjoint, positive semi-definite and normalized (its trace is equal to 1):

$$\rho^\dagger = \rho, \tag{2.2}$$

$$\rho \geq 0 \qquad \Leftrightarrow \qquad \langle \psi \,|\, \rho \,|\, \psi \rangle \geq 0 \quad \forall \, |\psi\rangle \in \mathbb{C}^n, \tag{2.3}$$

$$\mathrm{T}r\,\rho = 1. \tag{2.4}$$

The positivity and normalization of ρ guarantee that the eigenvalues of ρ are non-negative and smaller than (or equal to) 1, so that the spectral decomposition of ρ reads:

$$\begin{aligned} \rho &= \sum_i p_i \,|\phi_i\rangle \,\langle \phi_i| \,, \\ \mathrm{T}r\,\rho &= \sum_i p_i = 1, \end{aligned} \tag{2.5}$$

where $|\phi_i\rangle$ and p_i are the orthonormal eigenvectors and eigenvalues of ρ: $\rho\,|\phi_i\rangle = p_i\,|\phi_i\rangle$.

A special class of density matrices is formed by the *pure states*, i.e. projectors onto specific (normalized) vectors of $\mathbb{C}^n$:

$$\rho = |\psi\rangle \,\langle \psi|$$

which are idempotent ($\rho^2 = \rho$).

Any linear convex combination of projectors $\sum_j \mu_j \,|\psi_j\rangle\,\langle\psi_j|$ ($0 \leq \mu_j \leq 1$, $\sum_j \mu_j = 1$) is a density matrix fulfilling conditions (2.2), (2.3) and (2.4) and it is called *statistical mixture*. It is straightforward to notice that every linear convex combination of statistical mixtures is still a statistical mixture. We denote with $\mathcal{S}(S)$ the (convex) set of statistical mixtures. From the physical point of view the convexity of $\mathcal{S}(S)$ means that the density matrices description, based on the choice of a statistical ensemble of many copies of the system S, is still consistent if we take a mixture of statistical ensembles.

The need of generalizing the notion of states from pure state projectors to convex combinations of them comes from the effects of the quantum measurement processes.

The theory of measurement in Quantum Mechanics can be formulated in many different ways, the first one due to Von Neumann [17]. Even though more complicate descriptions have since been proposed, in the attempt to remove some of the unsatisfactory aspects of the original formulation, for our purpose the following scheme will be sufficient.

We will deal with open quantum systems with finite number of degrees of freedom, thus to every observable R is associated a self-adjoint operator with a discrete spectrum $\{\lambda_i\}$, that can be written with respect to its spectral family of orthogonal one-dimensional eigenprojectors

$$P_i \equiv |\psi_i\rangle\langle\psi_i|, \tag{2.6}$$
$$P_i P_j = \delta_{ij} P_i, \tag{2.7}$$
$$\sum_i P_i = \mathbf{1}, \tag{2.8}$$

as

$$R = \sum_j \lambda_j P_j, \quad \lambda_j \in \mathbb{R}. \tag{2.9}$$

According to the postulates of Quantum Mechanics, if the system S is in a pure state $\rho = |\psi\rangle\langle\psi|$, then the possible outcomes of the measurement of R are exactly its eigenvalues $\{\lambda_i\}$. Furthermore:

- the probability to get the outcome λ_i is $|\langle\psi_i\,|\,\psi\rangle|^2 = \langle\psi_i\,|\,\rho\,|\,\psi_i\rangle = \mathrm{Tr}(\rho P_i)$,
- if the measurement gives λ_i, then the post-measurement state is $P_i = |\psi_i\rangle\langle\psi_i|$.

Consequently, after repeating the measurement of R on many equally prepared copies of the system S, all described by the density matrix $|\psi\rangle\langle\psi|$, collecting all the resulting post-measurement states, the system has collapsed onto the state

$$\rho' = \sum_i \langle\psi_i\,|\,\rho\,|\,\psi_i\rangle\,|\psi_i\rangle\langle\psi_i| = \sum_i P_i \rho P_i. \tag{2.10}$$

The above process is then extended to any statistical mixture $\rho \in \mathcal{S}(S)$ by linearity.

2.1.1. Dynamics in density matrix formalism

In the density matrix formalism the Schrödinger equation translates into the Liouville-Von Neumann equation in $\mathbb{C}^n$

$$\partial_t \rho_t = -i[H, \rho_t].$$

Indeed, from the Schrödinger equation the time-evolution law is simply

$$|\psi(t)\rangle = U_t\,|\psi(0)\rangle \qquad |\psi(0)\rangle \text{ initial state},$$

where $U_t = e^{-iHt}$ is the unitary evolution operator.

This allows to derive the evolution law for a density matrix by linearity: starting from the initial state $\rho_0 = \sum_j \lambda_j |\psi_j\rangle \langle\psi_j|$, one gets $\rho_t = \sum_j \lambda_j |\psi_j(t)\rangle \langle\psi_j(t)|$, whence

$$\partial_t \rho_t = \sum_j \lambda_j (-iH |\psi_j(t)\rangle \langle\psi_j(t)| + i |\psi_j(t)\rangle \langle\psi_j(t)| H) = -i[H, \rho_t]. \tag{2.11}$$

The solution of the Liouville-Von Neumann equation is

$$\rho_t = U_t \rho_0 U_{-t} = e^{-iHt} \rho_0 e^{iHt} \tag{2.12}$$

The maps

$$\mathbb{U}_t \colon \rho_0 \mapsto U_t \rho_0 U_{-t}, \qquad t \in \mathbb{R} \tag{2.13}$$

form a one-parameter group of linear maps in $\mathcal{S}(S)$:

$$\mathbb{U}_t \circ \mathbb{U}_s = \mathbb{U}_{t+s}, \qquad t, s \in \mathbb{R}, \tag{2.14}$$

which is the hallmark of the *reversible* character of the dynamics of closed systems.

In terms of the generator $\mathbf{L}_H$

$$\mathbf{L}_H[\rho] \equiv -i[H, \rho],$$

$\mathbb{U}_t$ can be formally written as

$$\mathbb{U}_t = e^{t\mathbf{L}_H} = \sum_{k=0}^{\infty} \frac{t^k}{k!} \mathbf{L}_H^k.$$

Acting on $\mathcal{S}(S)$, $\mathbb{U}_t$ preserves the spectrum of all states ρ and transforms pure states into pure states.

2.2. Open quantum systems

Since the main object of study of the present work is the family of open quantum systems, it is necessary to briefly introduce the fundamentals of the quantum mechanical description of compound systems. In the following we will deal with a system S interacting with an *environment* which is characterized by a very large number of degrees of freedom. Calling $\mathcal{H}$ the environment Hilbert space, the Hilbert space of the total system $S + E$ is $\mathbb{C}^n \otimes \mathcal{H}$.

Moreover, if ρ_{S+E} is a generic state (density matrix) of the compound system, the statistical properties of the subsystem S are given by a density matrix ρ_S obtained by taking the *partial trace* over the degrees of freedom of E:

$$\rho_S \equiv \mathrm{Tr}_E(\rho_{S+E}). \tag{2.15}$$

This partial trace provides a reduced density matrix describing the state of the system S alone. Indeed, this is what results by considering mean values of observables $A_S \otimes \mathbf{1}_E$ on $\mathbb{C}^n \otimes \mathcal{H}$, as one can see by using an orthonormal basis $\left\{ \left| \psi_k^S \otimes \phi_\alpha^E \right\rangle_{k,\alpha} \right\}$ for $\mathbb{C}^n \otimes \mathcal{H}$:

$$\begin{aligned}
\mathrm{Tr}_{S+E}\left(\rho_{S+E} A_s \otimes \mathbf{1}_E\right) &= \sum_{k=1}^{n} \sum_{\alpha} \left\langle \psi_k^S \otimes \phi_\alpha^E \,\middle|\, (\rho_{S+E} \cdot A_S \otimes \mathbf{1}_E) \,\middle|\, \psi_k^S \otimes \phi_\alpha^E \right\rangle = & (2.16)\\
&= \sum_{k=1}^{n} \left\langle \psi_k^S \middle| \Big(\sum_{\alpha} \left\langle \phi_\alpha^E \,\middle|\, \rho_{S+E} \,\middle|\, \phi_\alpha^E \right\rangle \Big) A_S \middle| \psi_k^S \right\rangle = & (2.17)\\
&= \mathrm{Tr}_S\left(\mathrm{Tr}_E(\rho_{S+E}) A_S\right). & (2.18)
\end{aligned}$$

When we switch to a compound system $S+E$, which is closed if considered as whole, its time evolution is described by a group of dynamical maps

$$\mathbb{U}_t^{S+E} = e^{t\mathbf{L}_{S+E}}$$

on the state space $\mathcal{S}(S+E)$ of the density matrices ρ_{S+E}, where $\mathbf{L}_{S+E}$ is the generator of the overall dynamics, that it is assumed to be the sum of three generators:

$$\mathbf{L}_{S+E}^{\lambda} = \mathbf{L}_S + \mathbf{L}_E + \lambda \mathbf{L}'. \tag{2.19}$$

They are defined by the commutators

$$\begin{aligned}
\mathbf{L}_S[\rho_{S+E}] &= -i[H_S \otimes \mathbf{1}_E, \rho_{S+E}], & (2.20)\\
\mathbf{L}_E[\rho_{S+E}] &= -i[\mathbf{1}_S \otimes H_E, \rho_{S+E}], & (2.21)\\
\lambda \mathbf{L}'[\rho_{S+E}] &= -i\lambda[H', \rho_{S+E}]. & (2.22)
\end{aligned}$$

The Hamiltonian H' describes the interaction between the system and the environment whose strength is measured by the a-dimensional coupling λ.

From the density matrix ρ_{S+E} of the compound system, the statistical properties of the system S are derived by taking the *partial trace* over the degrees of freedom of E:

$$\rho_S(t) = \mathrm{Tr}_E\left(\mathbb{U}_t^{S+E}[\rho_{S+E}]\right). \tag{2.23}$$

The map

$$\mathbb{G}_t \colon \mathcal{S}(S) \ni \rho_S \mapsto \rho_S(t) = \mathrm{Tr}_E\left(\mathbb{U}_t^{S+E}[\rho_{S+E}]\right) \in \mathcal{S}(S)$$

is called *reduced dynamics* on the space of states $\mathcal{S}(S)$ of the open quantum system S.

It has been shown [18] that if one requires that the maps $\mathbb{G}_t$ preserve the convex structure of $\mathcal{S}(S)$, i.e.

$$\mathbb{G}_t\left[\sum_j \lambda_j \rho_S^j\right] = \sum_j \lambda_j \mathbb{G}_t[\rho_S^j]$$

then it is necessary that the initial state of the compound system be factorized:

$$\rho_{S+E} = \rho_S \otimes \rho_E, \tag{2.24}$$

where ρ_E is a fixed state of the environment.

The family of maps $\mathbb{G}_t$ is neither a one-parameter group nor a semigroup; namely we cannot expect $\mathbb{G}_t \circ \mathbb{G}_s = \mathbb{G}_{t+s}$ for $t, s \geq 0$, in general, because the partial trace operation can introduce irreversibility and memory effects.

In the following we will always consider factorized initial states for the compound system of the form $\rho_{S+E} = \rho_S \otimes \rho_E$.

By using the spectral representation of ρ_E, $\rho_E = \sum_j r_j^E \left|r_j^E\right\rangle \left\langle r_j^E\right|$, we can write

$$\begin{aligned}
\rho_S(t) &= \mathbb{G}_t[\rho_S] = \\
&= \mathrm{Tr}_E\left(\mathbb{U}_t^{S+E}[\rho_S \otimes \rho_E]\right) = \\
&= \sum_{j,k} r_k^E \left\langle r_j^E \,\middle|\, \left(U_t^{S+E} \rho_S \otimes \left|r_k^E\right\rangle \left\langle r_k^E\right|\right) U_{-t}^{S+E} \,\middle|\, r_j^E \right\rangle = \\
&= \sum_{j,k} W_{jk}(t) \rho_S W_{jk}^\dagger(t),
\end{aligned} \tag{2.25}$$

where $W_{jk}(t) = \sqrt{r_k^E}\left\langle r_j^E \,\middle|\, U_t^{S+E} \,\middle|\, r_k^E\right\rangle$ are operators on $\mathbb{C}^n$, i.e. elements of $M_n(\mathbb{C})$, that satisfy the relation

$$\sum_{j,k} W_{jk}^\dagger(t) W_{jk}(t) = \mathrm{Tr}(\rho_E U_{-t}^{S+E} U_t^{S+E}) = \mathbf{1}_n.$$

Given the unitary time-evolution one can always pass from the Schrödinger to the Heisenberg picture through the *duality relation*

$$\mathrm{Tr}\left[\mathbb{U}_t[\rho] X\right] = \mathrm{Tr}\left[\rho \mathbb{U}_t^*[X]\right], \qquad \forall \rho \in \mathcal{S}(S),\ X \in M_n(\mathbb{C}). \tag{2.26}$$

This defines the action of the *dual map* $\mathbb{U}_t^T$ on $X \in M_n(\mathbb{C})$:

$$X \mapsto \mathbb{U}_t^T[X] = U_{-t} X U_t = e^{-t\mathbb{L}}[X].$$

In the case of the reduced dynamics (2.25), the dual map of $\mathbb{G}_t$ is

$$M_n(\mathbb{C}) \ni X \mapsto \mathbb{G}_t^T[X] = \sum_{j,k} W_{jk}^\dagger(t) X W_{jk}(t) \in M_n(\mathbb{C}). \tag{2.27}$$

2.3. Positivity and complete positivity

Time-evolving density matrices must remain positive in order to keep their statistical meaning; therefore, any dynamical map $\rho \mapsto \mathbb{G}_t[\rho]$ describing the time-evolution from an initial state ρ to a state ρ_t at time $t \geq 0$ must preserve the positivity of ρ_t at all positive times. Namely:

$$\langle \psi \,|\, \mathbb{G}_t[\rho] \,|\, \psi \rangle \geq 0, \qquad \forall\, |\psi\rangle \in \mathbb{C}^n, \quad \forall \rho \in \mathcal{S}(S), \quad \forall t \geq 0. \tag{2.28}$$

Definition 1. We say that a linear map $\Lambda\colon M_n(\mathbb{C}) \to M_n(\mathbb{C})$ is *positive* if it sends positive matrices into positive matrices:

$$0 \leq X \mapsto \Lambda[X] \geq 0.$$

It is easy to check that $\mathbb{G}_t$ in (2.25) is indeed positive:

$$\langle \psi \,|\, \mathbb{G}_t[\rho_S] \,|\, \psi \rangle = \sum_{j,k} \left\langle \psi \,\middle|\, W_{jk}(t) \rho_S W_{jk}^\dagger(t) \,\middle|\, \psi \right\rangle \geq 0, \tag{2.29}$$

since ρ_S is positive definite.

While positivity is a necessary requirement for the physical consistency of the groups and semi-groups of dynamical maps, it is not sufficient to ensure a fully physical consistent behaviour when dealing with compound systems. In this case another stronger condition is required: *complete positivity*. In order to clarify this concept we consider, together with the n-dimensional system S, a second inert m-dimensional system A, called *ancilla*, that may have interacted with S in the past but has been decoupled from S at time $t = 0$. In this context "inert" means that A does not evolve anymore, even though statistical correlations might have been established between S and A, encoded in the initial state of the compound system $S + A$: $\rho_{S+A}(0)$.

Thus the kind of evolution we are considering for the compound system is described by a dynamical map of the form $\Lambda \otimes id_A$, where Λ acts on $M_n(\mathbb{C})$ and id_A is the identity action on $M_m(\mathbb{C})$. We can give the following definition:

Definition 2 (Complete Positivity)**.** A linear map $\Lambda\colon M_n(\mathbb{C}) \to M_n(\mathbb{C})$ is *completely positive* if $\Lambda \otimes id_m$ is positive on $M_n(\mathbb{C}) \otimes M_m(\mathbb{C})$ ("m-positive") for all $m \geq 1$.

Every completely positive map is also positive but the converse is not always true. Indeed, let us consider one qubit S, that is a two level system, with an ancilla $A = S$

and the transposition map:

$$T_2 \colon \begin{pmatrix} a & b \\ c & d \end{pmatrix} \to \begin{pmatrix} a & c \\ b & d \end{pmatrix} .$$

T_2 is a positive map because it does not alter the spectrum of operators. If we take the projector $P_+^{(2)} \equiv \left|\psi_+^{(2)}\right\rangle \left\langle \psi_+^{(2)}\right|$, onto the following state of $S+S$,

$$\left|\psi_+^{(2)}\right\rangle \equiv \frac{1}{\sqrt{2}}\Big(|0\rangle \otimes |0\rangle + |1\rangle \otimes |1\rangle \Big), \qquad |0\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix},$$

then $P_+^{(2)}$ is a 4×4 matrix with eigenvalues 0 and 1

$$P_+^{(2)} = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 1 \end{pmatrix} , \tag{2.30}$$

while

$$T_2 \otimes id_2[P_+^{(2)}] = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

has eigenvalues ± 1.

Namely, $T_2 \otimes id_2$ sends a positive matrix into a non-positive matrix, which means that T_2 is not even 2-positive and thus not completely positive.

The same considerations above can be extended to the projector on the totally symmetric state of $S+S$, where S is an n-level system:

$$P_+^{(n)} \equiv \left|\psi_+^{(n)}\right\rangle \left\langle \psi_+^{(n)}\right|, \qquad \left|\psi_+^{(n)}\right\rangle \equiv \frac{1}{\sqrt{n}} \sum_{j=1}^{n} |j\rangle \otimes |j\rangle ,$$

$\{|j\rangle\}_{j=1,\ldots,n}$ being an orthonormal basis in $\mathbb{C}^n$. The action of the *partial transposition* $T_n \otimes id_n$ on $P_+^{(n)}$ is given by

$$T_n \otimes id_n[P_+^{(n)}] = \frac{1}{n} \sum_{j,k=1}^{n} |k\rangle \langle j| \otimes |j\rangle \langle k|$$

and corresponds to the *flip operator* on $\mathbb{C}^n \otimes \mathbb{C}^n$

$$V\left(|\psi\rangle \otimes |\phi\rangle\right) = |\phi\rangle \otimes |\psi\rangle$$

that has eigenvalue -1 on any anti-symmetric state of $\mathbb{C}^n \otimes \mathbb{C}^n$.

Completely positive maps have been intensively studied since the seventies: a series of theorems have fixed some of their features and in particular their formal representation. Here we limit ourselves to summarize only the results which are essential for our aims, in a slightly different formulation with respect to the original one, that is more suited to our needs.

Theorem 1 (Choi [19])**.** *A linear map* $\Lambda\colon M_n(\mathbb{C}) \to M_n(\mathbb{C})$ *is* completely positive *if and only if it can be written in the form*

$$\Lambda[X] = \sum_\alpha W_\alpha^* X W_\alpha \qquad \textit{Kraus - Stinespring form.}$$

where $W_\alpha \in M_n(\mathbb{C})$ *and the sum extends at most* n^2 *terms.*

Looking at the expression of the map $t \mapsto \rho_S(t)$ in (2.25) in terms of the operators $W_{jk}(t)$, it is evident from the Kraus theorem that the reduced dynamics $\{\mathbb{G}_t\}_{t\geq 0}$ of open quantum systems consists of CP (completely positive) maps. Before going further, we want to underline another important feature of the CP maps: its tight relation with the concept of *entanglement*.

Definition 3 (Entanglement)**.** Given two state-spaces, $\mathcal{S}(S_1)$ and $\mathcal{S}(S_2)$ of two quantum ssytems S_1, S_2, a state $\rho_{S_1+S_2} \in \mathcal{S}(S_1 + S_2) \equiv \mathcal{S}(S_1) \otimes \mathcal{S}(S_2)$ is said *separable* if it can be written as a convex linear combination of product states $\rho_i^1 \otimes \rho_j^2$:

$$\rho_{S_1+S_2} = \sum_{i,j} \lambda_{ij} \rho_i^1 \otimes \rho_j^2, \qquad \lambda_{ij} \geq 0, \qquad \sum_{i,j} \lambda_{ij} = 1.$$

If it cannot be written as linear convex combinations of product states $\rho_i^1 \otimes \rho_j^2$, then it is called *entangled.*

The state $P_+^{(2)}$ introduced in (2.30) is an entangled state as well as the more general projector $P_+^{(n)}$.

The following theorems establish the connections between completely positive maps and entangles states of $S + S$, S an n-level system. [20]

Theorem 2. *A linear map* $\Lambda\colon M_n(\mathbb{C}) \to M_n(\mathbb{C})$ *is positive iff*

$$\left\langle \psi \otimes \phi \,\middle|\, \Lambda \otimes id_n(P_+^{(n)}) \,\middle|\, \psi \otimes \phi \right\rangle \geq 0 \qquad \forall \psi, \phi \in \mathbb{C}^n.$$

Theorem 3. *A linear map* $\Lambda\colon M_n(\mathbb{C}) \to M_n(\mathbb{C})$ *is completely positive iff*

$$\left\langle \psi \,\middle|\, \Lambda \otimes id_n[P_+^{(n)}] \,\middle|\, \psi \right\rangle \geq 0 \qquad \forall \psi \in \mathbb{C}^n \otimes \mathbb{C}^n.$$

Theorem 2 can be restated saying that Λ is positive if and only if $\mathrm{Tr}(\Lambda \otimes id_n[P_+^{(n)}]\rho) \geq 0$ for all separable density matrices ρ. Theorem 3 implies that if the map Λ is positive but not CP, then $\Lambda \otimes id_n[P_+^{(n)}]$ is not a positive matrix. This means that the totally symmetric projector $P_+^{(n)}$, which is a physically possible state for $S+S$, is not transformed into a physical state by $\Lambda \otimes id_n$.

Consequently completely positivity is a necessary requirement for the physical consistency of the evolution law of a system entangled with an ancilla.

Concretely: if a map is only positive, then there surely exists an entangled state ρ_{ent} of $S+S$ such that $\rho'_{ent} = \Lambda^T \otimes id_n[\rho_{ent}]$ has negative eigenvalues in order to make $\mathrm{Tr}(\rho'_{ent}P_+^{(n)}) < 0$.

2.4. Master Equation for the reduced dynamics

We have seen that maps of the form (2.25)

$$\rho_S \mapsto \mathbb{G}_t[\rho_S] = \sum_{j,k} W_{jk}(t)\rho_s W_{jk}^\dagger(t)$$

are completely positive and describe a physically consistent evolution of an open system S in contact with an environment E, provided that the initial state ρ_{S+E} of $S+E$ factorizes: $\rho_{S+E} = \rho_S \otimes \rho_E$.

A convenient expression for the differential equation describing such a time-evolution of the system state ρ_S (the *Master Equation*) can be very tricky to find out since the maps $\mathbb{G}_t$ carry memory effects due to the coupling between S and E. Nevertheless, under the assumption that the coupling is weak enough, one can find an approximated time-evolution law for S, determined by a one-parameter semi-group γ_t ($t \geq 0$). There are different ways to derive the Master Equation, each of them depending on the particular adopted approximation.

All of them will have the form:

$$\partial_t \rho_S(t) = (\mathbf{L}_H + \mathbf{D})[\rho_S(t)], \tag{2.31}$$

where $\mathbf{L}_H[\cdot] \equiv -i[H, \cdot]$ corresponds to the standard Schrödinger time-evolution due to a Hamiltonian H, while $\mathbf{D}$ is a linear operator on the space of states $\mathcal{S}(S)$ that encodes the noisy and dissipative effects of the environment, often called "*dissipator*".

Remark 2.1. It is worth to anticipate that the Hamiltonian H associated to the operator $\mathbf{L}_H$ in the Master Equation (2.31), is not, in general, the Hamiltonian H_S of the isolated system S. In particular, if (2.19) is the total generator for the compound system $S+E$, we will see that the action of the operator $\mathbf{L}_H$ will be given by an expression of the kind

$$\mathbf{L}_H[\rho_S] = \mathbf{L}_S[\rho_S] - i\lambda^2[H^{(1)}, \rho_S], \tag{2.32}$$

where $\mathbf{L}_S$ is the same as in (2.20), but with the addition of a *Lamb shift* correction, coming from the interaction with the environment, represented by an hermitian operator $H^{(1)}$ modulated by the square of the coupling factor, λ^2. $\square$

An immediate consequence of (2.31) is that the semigroup $\{\gamma_t\}_{t\geq 0}$ consists of the formal maps:

$$\gamma_t \rho_S = e^{t(\mathbf{L}_H + \mathbf{D})}\rho_S. \tag{2.33}$$

Interestingly the imposition of the basic requirements of physical consistency outlined above fixes the form of the generator $\mathbf{L}_H$. Indeed, asking for the maps γ_t to be completely positive and trace-preserving provides a Master Equation in the so called Gorini-Kossakowski-Sudarshan-Lindblad form[1]:

Theorem 4. *[21] Let $\gamma_t\colon M_n(\mathbb{C}) \to M_n(\mathbb{C})$, $t \geq 0$, form a time-continuous semigroup of completely positive trace-preserving linear maps. Then, $\gamma_t = exp(t(\mathbf{L}_H + \mathbf{D}))$, where the generators are given by*

$$\mathbf{L}_H[\rho] = -i[H,\, \rho] \tag{2.34}$$

$$\mathbf{D}[\rho] = \sum_{j,k=1}^{n^2-1} C_{jk}\left(V_k^\dagger \rho V_j - \frac{1}{2}\left\{V_j V_k^\dagger,\, \rho\right\}\right) \tag{2.35}$$

where the matrix of coefficients C_{jk} (Kossakowski matrix) *is non-negative, the V_j are orthogonal: $V_{n^2} = \mathbf{1}_n$, $Tr(V_j^\dagger V_k) = \delta_{jk}$, and $\{\cdot,\cdot\}$ denotes the anticommutator.*

Also the converse is true, namely:

Theorem 5. *[22], [21] A semigroup $\{\gamma_t\}_{t\geq 0} = e^{t(\mathbf{L}_H + \mathbf{D})}$ where $\mathbf{L}_H$ and $\mathbf{D}$ are of the form and* (2.34) *and* (2.35)*, as in the theorem above, consists of completely positive maps if and only if the Kossakowski matrix is positive definite.*

Example 1. Thanks to Theorem 5 we can better understand the importance of completely positivity with the following example, which makes use of the CP check on the Kossakowski matrix.

[1]The original formulation was given in the dual representation of the algebra $M_n(\mathbb{C})$

Consider for a qubit state

$$\rho = \frac{1}{2}\begin{pmatrix} 1+r_3 & r_1 - ir_2 \\ r_1 + ir_2 & 1-r_3 \end{pmatrix} \qquad r_1, r_2, r_3 \in \mathbb{R}, \quad r_1^2 + r_2^2 + r_3^2 \leq 1, \tag{2.36}$$

the following time-evolution ($T_1, T_2 > 0$):

$$\rho \mapsto \rho_t = \frac{1}{2}\begin{pmatrix} 1 + r_3 e^{-t/T_1} & (r_1 - ir_2)e^{-t/T_2} \\ (r_1 + ir_2)e^{-t/T_2} & 1 - r_3 e^{-t/T_1} \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1 + r_3(t) & r_1(t) - ir_2(t) \\ r_1(t) + ir_2(t) & 1 - r_3(t) \end{pmatrix}. \tag{2.37}$$

Clearly, $r_1^2(t) + r_2^2(t) + r_3^2(t) \leq 1$ so that any initial state is mapped into another state at time t, its spectrum being always non-negative.

Using the *Bloch representation* with respect to the Pauli matrices

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{2.38}$$

one finds

$$\frac{\mathrm{d}\rho_t}{\mathrm{d}t} = -\frac{1}{2}\left(\frac{e^{-t/T_2}}{T_2}(r_1\sigma_1 + r_2\sigma_2) + \frac{e^{-t/T_1}}{T_1} r_3\sigma_3\right). \tag{2.39}$$

This equals the action of the generator

$$\mathbf{L}[\rho_t] = \frac{1}{4T_1}(\sigma_1\rho_t\sigma_1 - \rho_t) + \frac{1}{4T_1}(\sigma_2\rho_t\sigma_2 - \rho_t) + \left(\frac{1}{2T_2} - \frac{1}{4T_1}\right)(\sigma_3\rho_t\sigma_3 - \rho_t), \tag{2.40}$$

as one can check by considering that

$$\mathbf{L}[\sigma_1] = -\frac{\sigma_1}{T_2}, \quad \mathbf{L}[\sigma_2] = -\frac{\sigma_2}{T_2}, \quad \mathbf{L}[\sigma_3] = -\frac{\sigma_3}{T_1}. \tag{2.41}$$

The Kossakowski matrix of this generator is

$$C = \frac{1}{4}\begin{pmatrix} \frac{1}{T_1} & 0 & 0 \\ 0 & \frac{1}{T_1} & 0 \\ 0 & 0 & \frac{2}{T_2} - \frac{1}{T_1}. \end{pmatrix} \tag{2.42}$$

Thus, the semigroup $\gamma_t = e^{t\mathbf{L}}$ consists of completely postive maps if and only if

$$\frac{2}{T_2} - \frac{1}{T_1} \geq 0 \Leftrightarrow 2T_1 \geq T_2. \tag{2.43}$$

Let us now couple the open qubit to another inert qubit so that their common time-evolution is given by $\gamma_t \otimes \mathrm{id}$. Given the completely symmetric entangled initial state

$$|\psi\rangle_{S+S} = \frac{|00\rangle + |11\rangle}{\sqrt{2}} \quad \text{where} \quad \sigma_3 |0\rangle = |0\rangle \, , \, \sigma_3 |1\rangle = -|1\rangle \, , \tag{2.44}$$

after writing

$$|\psi\rangle \langle\psi|_{S+S} = \frac{1}{4}[\mathbf{1} \otimes \mathbf{1} + \sigma_1 \otimes \sigma_1 - \sigma_2 \otimes \sigma_2 + \sigma_3 \otimes \sigma_3], \tag{2.45}$$

one finds

$$\gamma_t \otimes id \left[|\psi\rangle \langle\psi|_{S+S}\right] = \frac{1}{4}\left[\mathbf{1} \otimes \mathbf{1} + e^{-t/T_2}(\sigma_1 \otimes \sigma_1 - \sigma_2 \otimes \sigma_2) + e^{-t/T_1}\sigma_3 \otimes \sigma_3\right]. \tag{2.46}$$

As a 4×4 matrix this operator reads

$$\gamma_t \otimes id \left[|\psi\rangle \langle\psi|_{S+S}\right] = \frac{1}{4}\begin{pmatrix} 1 + e^{-t/T_1} & 0 & 0 & 2e^{-t/T_2} \\ 0 & 1 - e^{-t/T_1} & 0 & 0 \\ 0 & 0 & 1 - e^{-t/T_1} & 0 \\ 2e^{-t/T_2} & 0 & 0 & 1 + e^{-t/T_1} \end{pmatrix}. \tag{2.47}$$

It has eigenvalues $\lambda_1(t) = 1 - e^{-t/T_1}$ (twice degenerate), $\lambda_2(t) = 1 + e^{-t/T_1} + 2e^{-t/T_2}$ and $\lambda_3(t) = 1 + e^{-t/T_1} - 2e^{-t/T_2}$.

For small times $\lambda_3(t) \sim 1 + 1 - t/T_1 - 2 + 2t/T_2 = t\left(\frac{2}{T_2} - \frac{1}{T_1}\right)$ remains positive if and only if $T_2 \leq 2T_1$ that is if and only if the maps γ_t are completely positive. □

The standard procedure to derive the Master Equation is a technique based on the use of projection operators on the overall state-space $\mathcal{S}(S+E)$. In particular one defines

$$\mathbf{P}\rho_{S+E} \equiv \mathrm{Tr_E}[\rho_{S+E}] \otimes \rho_E = \rho \otimes \rho_E \tag{2.48}$$

by the *partial trace* operation over the environment degrees of freedom, ρ_E being a suitable equilibrium environment state: $\mathbf{L}_E[\rho_E] = -i[H_E, \rho_E] = 0$. In most cases of interest ρ_E is nothing but the thermal Gibbs equilibrium state. Indeed, usually E is taken to be a *thermal bath*, i.e. a system that is so large that it is left untouched by the interaction with the smaller system S and consequently stays in its equilibrium state.

Notice that $\mathbf{P}$ acts projectively on $\mathcal{S}(S)$: $\mathbf{P}^2\rho_{S+E} = \mathbf{P}\rho\otimes\rho_E$, with orthogonal projector $\mathbf{Q} \equiv \mathbf{1}_{S+E} - \mathbf{P}$.

Let us consider the global reversible time-evolution equation

$$\partial_t\rho_{S+E}(t) = \mathbf{L}^{\lambda}_{S+E}[\rho_{S+E}(t)], \tag{2.49}$$

for the compound system $S + E$ with generator as in (2.19).

Using $\mathbf{P}$ and $\mathbf{Q}$ one can split the above equation:

$$\partial_t \mathbf{P}\rho_{S+E}(t) = \mathbf{L}_{S+E}^{PP}\left[\mathbf{P}\rho_{S+E}(t)\right] + \mathbf{L}_{S+E}^{PQ}\left[\mathbf{Q}\rho_{S+E}(t)\right]; \tag{2.50}$$

$$\partial_t \mathbf{Q}\rho_{S+E}(t) = \mathbf{L}_{S+E}^{QP}\left[\mathbf{Q}\rho_{S+E}(t)\right] + \mathbf{L}_{S+E}^{QQ}\left[\mathbf{Q}\rho_{S+E}(t)\right], \tag{2.51}$$

where $\mathbf{L}_{S+E}^{PP} \equiv \mathbf{P}\circ\mathbf{L}_{S+E}\circ\mathbf{P}$, $\mathbf{L}_{S+E}^{QQ} \equiv \mathbf{Q}\circ\mathbf{L}_{S+E}\circ\mathbf{Q}$, $\mathbf{L}_{S+E}^{PQ} \equiv \mathbf{P}\circ\mathbf{L}_{S+E}\circ\mathbf{Q}$, and $\mathbf{L}_{S+E}^{QP} \equiv \mathbf{Q}\circ\mathbf{L}_{S+E}\circ\mathbf{P}$.

The latter equation can be formally integrated, yelding:

$$\begin{aligned}\mathbf{Q}\rho_{S+E}(t) &= e^{t\mathbf{L}_{S+E}^{QQ}}\left[\mathbf{Q}\rho_S\otimes\rho_E\right] + \int_0^t \mathrm{d}s\, e^{(t-s)\mathbf{L}_{S+E}^{QQ}}\circ\mathbf{L}_{S+E}^{QP}\left[\mathbf{P}\rho_{S+E}(s)\right] = \\ &= \int_0^t \mathrm{d}s\, e^{(t-s)\mathbf{L}_{S+E}^{QQ}}\circ\mathbf{L}_{S+E}^{QP}\left[\mathbf{P}\rho_{S+E}(s)\right].\end{aligned}$$

Indeed $\mathbf{Q}\rho_S\otimes\rho_E = 0$.

Inserting this expression into (2.50), one obtains:

$$\partial_t\rho_S(t)\otimes\rho_E = \mathbf{L}_{S+E}^{PP}[\rho_S(t)\otimes\rho_E] + \int_0^t \mathrm{d}s\,\mathbf{L}_{S+E}^{PQ}\circ e^{(t-s)\mathbf{L}_{S+E}^{QQ}}\circ\mathbf{L}_{S+E}^{QP}\left[\rho_S(s)\otimes\rho_E\right]. \tag{2.52}$$

At this point we can trace out the environment taking into account that ρ_E is an equilibrium state for the environment E.

The interaction Hamiltonian H' in (2.22) can always be written in the form

$$H' = \sum_\alpha S_\alpha\otimes R_\alpha, \tag{2.53}$$

where S_α and R_α are hermitian operators on the system S and the environment E, respectively.

Moreover, one can always assume $\mathrm{Tr}(\rho_E R_\alpha) = 0$, a condition always obtainable by a suitable redefinition of R_α that only redefines the system Hamiltonian H_S.

A typical environment is a system consisting of infinitely many free bosons described by bosonic creation and annihilation operators $a_\alpha^\dagger$, a_α: $[a_\alpha, a_{\alpha'}^\dagger] = \delta_{\alpha\alpha'}$. Operators R_α are usually assumed to be field operators of the type:

$$R_\alpha = f_\alpha\left(a_\alpha^\dagger + a_\alpha\right),$$

where f_α is an energy density function. After some manipulations, the final Master Equation for the reduced dynamics reads[2]:

$$\partial_t \rho_S(t) = \mathbf{L}_S[\rho_S(t)] + \lambda^2 \int_0^t \mathrm{d}s\, \mathrm{Tr_E}\Big(\mathbf{L}' \circ e^{(t-s)\mathbf{L}_{S+E}^{QQ}} \circ \mathbf{L}'[\rho_S(s) \otimes \rho_E]\Big), \tag{2.54}$$

where $\mathbf{L}'$ is the interaction generator (2.22).

This generalized Master Equation is exact and free of any approximation. Its first derivation dates back to Nakajima [23] and Zwanzig [24]. Starting from the integro-differential equation, which clearly contains memory terms, different approximations can be performed in order to obtain a Markovian evolution of the form:

$$\rho_S(t) = e^{(\mathbf{L}_S + \lambda^2 \mathbf{K})t} \rho_S(0), \tag{2.55}$$

where $\mathbf{K}$ is some kind of generator to be determined.

2.4.1. Weak coupling limit in the Markovian approximation

The hypothesis of *weak coupling* between the system and the environment lies in the assumption that the typical decay time-scales of the two systems largely differ: in particular, if τ_E is the environment decay time-scale (i.e. roughly speaking the time needed to reach the equlilibrium) and τ_S the system evolution time-scale, then the ratio τ_E/τ_S must be very small. Practically speaking the idea is to introduce the slow time-scale $\tau \equiv \lambda^2 t$ and to let λ go to zero. Indeed, it is evident that the dissipative action of the second term in (2.54) becomes relevant only for $t \sim \lambda^{-2}$.

The simplest and most used approximation in literature is based on the substitution of the integral in (2.54) with

$$\lambda^2 \int_0^{+\infty} \mathrm{d}s\, \mathrm{Tr_E}\{\mathbf{L}' \circ e^{(\mathbf{L}_S + \mathbf{L}_E)s} \circ \mathbf{L}'[\rho_S(t) \otimes \rho_E]\} \tag{2.56}$$

which corresponds to a choice of the generator $\mathbf{K}$ given by

$$\mathbf{K}_1[\rho_S] = \int_0^{+\infty} \mathrm{d}s\, \mathrm{Tr_E}\{\mathbf{L}' \circ e^{(\mathbf{L}_S + \mathbf{L}_E)s} \circ \mathbf{L}'[\rho_S \otimes \rho_E]\}. \tag{2.57}$$

---

[2]Details in Appendix A

The idea behind this approximation is to rewrite the second term in (2.54) as

$$\int_0^t \mathrm{d}s\, \mathrm{Tr_E}\Big(\mathbf{L}' \circ e^{s\mathbf{L}^{QQ}_{S+E}} \circ \mathbf{L}'[\rho_S(t-s) \otimes \rho_E]\Big) =$$

$$= \int_0^{\tau/\lambda^2} \mathrm{d}s\, \mathrm{Tr_E}\Big(\mathbf{L}' \circ e^{s\mathbf{L}^{QQ}_{S+E}} \circ \mathbf{L}'\left[\rho_S\left(\frac{\tau}{\lambda^2} - s\right) \otimes \rho_E\right]\Big), \quad (2.58)$$

so that, when $\lambda \to 0$, one can extend the integration to $+\infty$ and replace $\rho_S(\tau/\lambda^2 - s)$ by $\rho_S(\tau/\lambda^2)$.

Despite its popularity this approximation is quite rough and in general leads to reduced dynamics that are not even positive preserving, let alone being completely positive. It can be refined starting from the integral version of the Master Equation (2.54)[3]:

$$\rho_S(t) = e^{t\mathbf{L}_S}\rho_S(0) + \lambda^2 \int_0^t \mathrm{d}s \int_0^s \mathrm{d}u\, e^{\mathbf{L}_S(t-s)} \mathrm{Tr_E}\{\mathbf{L}' \circ e^{(\mathbf{L}^{QQ}_{S+E})(s-u)} \circ \mathbf{L}'[\rho_S(u) \otimes \rho_E]\} \quad (2.59)$$

With a suitable change of integration variables it can be recast in the form

$$\rho_S(t) = e^{t\mathbf{L}_S}\rho_S(0) + \lambda^2 \int_0^t \mathrm{d}u\, e^{(t-u)\mathbf{L}_S} \left\{ \int_0^{t-u} \mathrm{d}v\, e^{-v\mathbf{L}_S} \mathrm{Tr_E}(\mathbf{L}' \circ e^{v(\mathbf{L}_{S+E})} \circ \mathbf{L}'[\rho_S(u) \otimes \rho_E]) \right\}. \quad (2.60)$$

By the same arguments as before, by going to $\tau = t\lambda^2$ and letting $\lambda \to 0$, one replaces the term in curly brackets with

$$\mathbf{K}_2[\rho_S(t)] = \int_0^{+\infty} \mathrm{d}v\, e^{-v\mathbf{L}_S} \mathrm{Tr_E}\big(\mathbf{L}' \circ e^{v(\mathbf{L}_S + \mathbf{L}_E)} \circ \mathbf{L}'[\rho_S(u) \otimes \rho_E]\big), \quad (2.61)$$

which corresponds to a Master Equation of the form

$$\partial_t \rho_S(t) = \mathbf{L}_S[\rho_S(t)] + \lambda^2 \mathbf{K}_2[\rho_S(t)]. \quad (2.62)$$

This is known as *Redfield equation*, with formal solution

$$\rho_S(t) = e^{t(\mathbf{L}_S + \lambda^2 \mathbf{K}_2)}\rho_S(0). \quad (2.63)$$

Again, it can be shown that the semigroup generated by (2.62) does not in general consists even of positive maps. Consequently a better approximation is needed; this is constructed as follows.

[3] See in particular Davies's works [25],[26]

One formally integrates the Redfield equation (2.62):

$$\rho_S(t) = e^{t\mathbf{L}_S}\rho_S(0) + \lambda^2 \int_0^t \mathrm{d}s\, e^{(t-s)\mathbf{L}_S}\mathbf{K}_2 e^{s(\mathbf{L}_S+\lambda^2\mathbf{K}_2)}\rho_S(0).$$

Then, one goes to $\tau = \lambda^2 t$ and switches to the *Interaction Picture*

$$\rho_S \mapsto e^{iH_S\frac{\tau}{\lambda^2}}\rho_S e^{-iH_S\frac{\tau}{\lambda^2}} = e^{-\frac{\tau}{\lambda^2}\mathbf{L}_S}\rho_S, \tag{2.64}$$

so that

$$\begin{aligned} e^{-\frac{\tau}{\lambda^2}\mathbf{L}_S}e^{\frac{\tau}{\lambda^2}(\mathbf{L}_S+\lambda^2\mathbf{K}_2)}\rho_S(0) = \rho_S(0)+ \\ + \int_0^\tau \mathrm{d}s\, \left\{ e^{-\frac{s}{\lambda^2}\mathbf{L}_S}\mathbf{K}_2 e^{\frac{s}{\lambda^2}\mathbf{L}_S}\right\} e^{-\frac{s}{\lambda^2}\mathbf{L}_S}e^{\frac{s}{\lambda^2}(\mathbf{L}_S+\lambda^2\mathbf{K}_2)}\rho_S(0). \end{aligned} \tag{2.65}$$

It has been shown by Davies [25–27] that, in the limit $\lambda \to 0$, only the non-oscillating terms survive and the operator in curly brackets can be substituted by the *ergodic average*:

$$\mathbf{K}_3[\rho] \equiv \lim_{T\to\infty}\frac{1}{2T}\int_{-T}^{+T}\mathrm{d}t\, e^{-t\mathbf{L}_S}\mathbf{K}_2 e^{t\mathbf{L}_S}\rho. \tag{2.66}$$

Now, setting $\gamma_\tau \equiv \lim_{\lambda\to 0} e^{-\frac{\tau}{\lambda^2}\mathbf{L}_S}e^{\frac{\tau}{\lambda^2}(\mathbf{L}_S+\lambda^2\mathbf{K}_2)}$, we have $\partial_t\gamma_t\rho_S(0) = \mathbf{K}_3[\gamma_t\rho_S(0)]$. By noticing that $\mathbf{K}_3 e^{-\frac{\tau}{\lambda^2}\mathbf{L}_S} = e^{-\frac{\tau}{\lambda^2}\mathbf{L}_S}\mathbf{K}_3$, going from τ/λ^2 back to t, one gets another Markovian Master Equation:

$$\partial_t\rho_S(t) = (\mathbf{L}_S + \lambda^2\mathbf{K}_3)[\rho_S(t)]. \tag{2.67}$$

In the end we have derived three different Master Equations. It is worth discussing which of them is the best candidate to describe physically consistent time-evolutions. Again, we will summarize Davies's results [25–27] following [28].

Let γ_t^λ denote the operator mapping the initial state $\rho_S(0)$ into the state evoluted at time t:

$$\gamma_t^\lambda\rho_S(0) = \mathrm{Tr}_{\mathrm{E}}\Big(e^{-t\mathbf{L}^\lambda_{S+E}}\,\rho_S(0)\otimes\rho_E\, e^{t\mathbf{L}^\lambda_{S+E}}\Big) \tag{2.68}$$

and let us introduce the environment *time correlators*

$$F_{\alpha\beta}(t) \equiv \mathrm{Tr}_{\mathrm{E}}(e^{itH_E}R_\alpha e^{-itH_E}R_\beta\rho_E). \tag{2.69}$$

Then, in the hypothesis that for some $\delta > 0$

$$\int_0^{+\infty}\mathrm{d}t\,|F_{\alpha\beta}(t)|(1+t)^\delta < +\infty,$$

we have the following results

$$\begin{cases} \lim\limits_{\lambda\to 0} \sup\limits_{0\le\lambda^2 t\le\tau} \|\gamma_t^\lambda \rho_S(0) - e^{(\mathbf{L}_S+\lambda^2\mathbf{K}_2)t}\rho_S(0)\| = 0; \\ \lim\limits_{\lambda\to 0} \sup\limits_{0\le\lambda^2 t\le\tau} \|\gamma_t^\lambda \rho_S(0) - e^{(\mathbf{L}_S+\lambda^2\mathbf{K}_3)t}\rho_S(0)\| = 0; \end{cases} \tag{2.70}$$

in the trace norm. But this result is not true, in general, if we put $\mathbf{K}_1$ in place of $\mathbf{K}_2$ or $\mathbf{K}_3$. Consequently the solution of (2.67) converges to the real reduced dynamics (2.68) in the limit $\lambda \to 0$, at any finite time, while the reduced dynamics generated by $\mathbf{K}_1$ do not always converge to the same map.

Dümcke and Spohn [28] proved that, except for some trivial cases, the generators $\mathbf{K}_1$ and $\mathbf{K}_2$ do not preserve positivity: this rules them out as reliable descriptions of proper, physically consistent time-evolutions.

On the other hand, $\mathbf{K}_3$ is such that the solutions of (2.67) are completely positive.

In order to prove this assertion, it is convenient to develop the action of operator $\mathbf{K}_3$ on a generic state ρ. The details are given in A.2. We have

$$\mathbf{K}_3[\rho] = \sum_\omega \sum_{\beta,\alpha} \hat{F}_{\beta\alpha}(-\omega)\left(S_\alpha^\dagger(\omega)\rho S_\beta(\omega) - \frac{1}{2}\left\{S_\beta(\omega)S_\alpha^\dagger(\omega),\, \rho\right\}\right) - i[H^{(1)},\, \rho]. \tag{2.71}$$

Here $\{S_\alpha(\omega)\}$ are the components of the Fourier expansion of the operators $\{S_\alpha\}$ written in the interaction picture:

$$S_\alpha(t) = e^{iH_S t} S_\alpha e^{-iH_S t} = \sum_\omega e^{it\omega} S_\alpha(\omega), \tag{2.72}$$

while $H^{(1)}$ is a self-adjoint operator acting as a correction, modulated by the arbitrary small coupling λ^2, to the system Hamiltonian H_S. $\hat{F}_{\alpha\beta}(\omega)$ are the Fourier components of the bath correlators in (2.69):

$$\hat{F}_{\alpha\beta}(\omega) = \int_{-\infty}^{+\infty} \mathrm{d}t\, e^{-it\omega} F_{\alpha\beta}(t). \tag{2.73}$$

We can now justify the remark in 2.1, where we anticipated that the general structure of the Master Equation has the form (2.31). Indeed, with the definitions

$$\mathbf{D}[\rho] \equiv \lambda^2 \sum_\omega \sum_{\beta,\alpha} \hat{F}_{\beta\alpha}(-\omega)\left(S_\alpha^\dagger(\omega)\rho S_\beta(\omega) - \frac{1}{2}\left\{S_\beta(\omega)S_\alpha^\dagger(\omega),\, \rho\right\}\right), \tag{2.74}$$

$$\mathbf{L}_H[\rho] \equiv -i[H_S, \rho] - i\lambda^2[H^{(1)}, \rho], \tag{2.75}$$

the Master Equation (2.67) can be rewritten as

$$\partial_t \rho_S(t) = (\mathbf{L}_H + \mathbf{D})[\rho_S(t)]. \tag{2.76}$$

In A.3 it is shown that the Kossakowski-Lindblad matrix in (2.71) is positive, hence the reduced dynamics generated by $\mathbf{K}_3$ is completely positive.

2.5. Conclusions

We summarize here the main concepts and results of this chapter.

- The time-evolution of an open quantum system in contact with a thermal environment is described by a *reduced dynamics* obtained from the dynamics of the whole system by *partial tracing over the environment degrees of freedom.*
- In order to be physically consistent, i.e. in order to preserve the quantum statistical meaning of the time-evoluted states, the reduced dynamics must be *completely positive*, which is a stronger condition than *positivity* alone. While the latter corresponds to keeping the positivity of the spectrum of time-evolving density matrices, only the former guarantees a similar robustness against coupling with ancillas.
- The reduced dynamics can be determined, as a *Markovian approximation*, under the assumnption of *weak coupling limit* and *factorization of the initial state* of the total system, by deriving a *Master Equation* for the reduced dynamics of the open quantum system alone.
- Master Equations can be derived within different levels of approximations: some of them do not give rise to completely-positive (not even positive) dynamical maps or their solutions do not converge to the real reduced dynamics in the limit of arbitrary small couplings.
- It is always possible to formulate a Master Equation fulfilling the requirement of complete positivity and which converges to the real reduced dynamics when the coupling strength goes to zero.

In the fourth chapter we will see a direct application of these ideas to a concrete physical model.

Chapter 3.

Thermodynamics of Open Quantum Systems

In the previous chapter it was discussed how lack of the specific requirement of complete positivity in the dynamical semigroup arising from a given Master Equation can lead to results that conflict with the "real", i.e. non approximated, reduced dynamics. Practically speaking, if the reduced dynamics γ_t of the system S is not completely positive, then there surely exists an entangled initial state ρ^{ent}_{S+S} of the system S coupled with an ancilla $A = S$ such that $\gamma_t \otimes id[\rho^{\text{ent}}_{S+S}]$ develops negative eigenvalues ad loses its meaning as a physical state.

In this chapter we will see how the complete positivity requirement can also avoid violations of the Second Law of Thermodynamics, which states (in one of its formulations) that internal entropy can never decrease. To prove this relation we need to introduce a formulation of the Second Law in the context of open quantum systems, conveniently defining the entropy function and a quantity called *entropy production*.

We start by summarizing the Classical Laws of Thermodynamics and then extend them to quantum systems.

3.1. Laws of Classical Thermodynamics

The Zero Law of Thermodynamics deals with the intuitive concepts of *thermal equilibrium* and *heat* and the related idea of *temperature*.

Definition 4. *Zero Law of Thermodynamics.* Two systems are in thermal equilibrium with each other if, when put into direct contact and heat exchange is allowed, nothing changes macroscopically.

As an experimental fact, we also know that when two bodies at different temperatures are allowed to exchange heat, the latter flows from the higher temperature body to the lower temperature body.

The First Law of Thermodynamics is essentially the statement of energy conservation. Given a system S in interaction with one or more thermal reservoirs (the environment), once we have established suitable operative definitions of

- *Internal Energy* E;
- *Work* W performed by the system on the environment;
- *Heat* Q transferred from the environment to the system;

we can give the formulation of the First Law:

Definition 5. *First Law of Thermodynamics.*

$$\mathrm{d}E = \delta Q - \delta W. \tag{3.1}$$

All these quantities have the dimension of energy. A positive δQ corresponds to an increase of internal energy E of the system while a positive δW produces a decrease of it.

We also note the different notation to distinguish the exact differential, expressed with d, from the infinitesimal variation of work and heat, expressed with δ: internal energy can be defined as a function of the state of the system, intended as a set of macroscopic observables that describe it completely, while the work and the heat exchanged always depend on the particular transformation that the system is undergoing. So, while after a transformation affecting the system the variation of its internal energy $\mathrm{d}E$ depends only on the initial and final macroscopic states, the amount of work and heat exchanged with the environment depends on the particular path followed during the transformation.

The Second Law of Thermodynamics has different formulations. Here we will use a formulation which makes use of the concept of *entropy*. In classical thermodynamics entropy is defined as follows. One says that the transformation of a system in contact with an environment is *quasi-static* if it is slow enough that at any time the system is in thermal equilibrium with the environment.

Definition 6. *Entropy in classical thermodynamics.* The variation of *entropy* in a system evolving from a state A to a state B in a *quasi-static* process is given by

$$S_{A,B} \equiv \int_A^B \frac{\delta Q}{T}. \tag{3.2}$$

Hence the expression for the differential entropy can be written

$$\mathrm{d}S = \frac{\delta Q}{T}. \tag{3.3}$$

With respect to this definition of entropy, the Second Law can be formulated as follows

Definition 7. *Second Law of Thermodynamics.* In every closed and isolated system the entropy never decreases.

In general the entropy of an open system can vary due to its interaction with the environment or because of its internal dynamics. So we can separate the variation $\mathrm{d}S$ into two contributions:

$$\mathrm{d}S = \mathrm{d}S_{\text{ext}} + \mathrm{d}S_{\text{int}}. \tag{3.4}$$

If we consider a system interacting with N thermal baths each at temperature T_i, $i = 1, \ldots, N$, then the external contribution to the entropy variation reads

$$\mathrm{d}S_{\text{ext}} = \sum_{i=1}^{N} \frac{\delta Q_i}{T_i}. \tag{3.5}$$

For a closed and isolated system $\delta Q_i = 0$, $\forall i$ and therefore $\mathrm{d}S_{\text{ext}} = 0$. The Second Law implies

$$\mathrm{d}S_{\text{int}} \geq 0. \tag{3.6}$$

3.2. The laws of thermodynamics in open quantum systems

Consider an open quantum system in interaction with N thermal reservoirs each at temperature $T_i = 1/(\kappa_B \beta_i)$ (κ_B being the Boltzmann constant). Let be H_0 the Hamiltonian of the system and for simplicity let its spectrum be discrete and finite. If the interaction with the environment is weak and the Markovian approximation is valid then the reduced dynamics of the system can be described by means of the Master Equation

$$\partial_t \rho(t) = -i[H_0, \rho(t)] + \sum_{m=1}^{N} \mathbf{D}_m[\rho(t)], \tag{3.7}$$

where the linear operators $\mathbf{D}_m$ are assumed to be of the Kossakowski-Lindblad (2.35) form and to satisfy the completely positivity condition. Furthermore we assume that for every bath there exists a stationary state ρ_m^{eq} of the system in thermal equilibrium with the bath, which is a Gibbs state of the form:

$$\rho_m^{\text{eq}} = \frac{e^{-\beta_m H_0}}{\mathrm{Tr}(e^{-\beta_m H_0})}. \tag{3.8}$$

Since $-i[H_0, \rho_m^{\rm eq}] = 0$, the stationarity requirement for $\rho_m^{\rm eq}$ corresponds to the condition

$$\mathbf{D}_m[\rho_m^{\rm eq}] = 0. \tag{3.9}$$

If there exists a unique bath then the thermal state $\rho_m^{\rm eq}$ is stationary for the overall dynamics and eq. (3.9) can be viewed as a formulation of the zeroth Law of Thermodynamics for open quantum systems.

Next we can consider a slightly more complicated scenario in which the system can produce some kind of mechanical work. For this aim we introduce a family of explicitly time-dependent self-adjointed operators $\{h_t; t \geq 0\}$ on the system Hilbert space. Consequently, since the new Hamiltonian has become time-dependent

$$H(t) = H_0 + h_t, \tag{3.10}$$

also the dissipators have become time-dependent: $\mathbf{D}_m = \mathbf{D}_m(t)$. Even though this may seem a potential problem, since an explicitly time-dependent Master Equation cannot be immediately integrated in an exponential map, there is another condition, which can be considered fulfilled in many cases of interest, that allow us to apply the same considerations above and to give a formulation of the Zero Law of Thermodynamics. Indeed it is not too restrictive to assume that the time scale τ_W at which h_t changes is much longer than the typical time scale required for a bath to thermalize, τ_B. So at any time t' in a time interval Δt such that $\tau_B \ll \Delta t \ll \tau_W$, $h_{t'}$ can be considered nearly constant as in a quasi-static process. Under these conditions the derivation of the Markovian Master Equation discussed in the first chapter is still valid and we can state the

Definition 8. *Zero Law of Thermodynamics for open quantum systems.* Let a system be subjected to the time-varying Hamiltonan $H(t)$ and interact with N thermal baths, whose dissipative actions are given by the operators $\{\mathbf{D}_m(t)\}_{m=1}^N$. Then, the dynamics of the system is governed by the Master Equation

$$\partial_t \rho(t) = -i[H(t),\, \rho(t)] + \sum_{m=1}^{N} \mathbf{D}_m(t)[\rho(t)], \tag{3.11}$$

and the Zero Law of Thermodynamics is embodied by the following two requirements

- $\rho_m^{\rm eq}(t) = \frac{e^{-\beta_m H(t)}}{Tr e^{-\beta_m H(t)}}$,
- $\mathbf{D}_m(t)[\rho_m^{\rm eq}(t)] = 0$.

In order to give a quantum formulation of the First Law we need to give the definition of *internal energy.*[1]

Definition 9. *Internal energy.* The internal energy of a quantum system whose state at time t is described by the density matrix $\rho(t)$ is the expectation value of the Hamiltonian

[1]The following definitions and the formulations of the I and II Laws are given following [29].

$H(t)$ on this state:

$$E(t) \equiv \langle H(t) \rangle_\rho = Tr(\rho(t)H(t)). \tag{3.12}$$

Coherently, the work performed by the system in an infinitesimal transformation is given by

$$\delta W(t) \equiv -Tr\left(\rho(t)\frac{\mathrm{d}h_t}{\mathrm{d}t}\right)\mathrm{d}t, \tag{3.13}$$

while the infinitesimally exchanged heat has the expression

$$\delta Q(t) \equiv Tr\left(\frac{\mathrm{d}\rho(t)}{\mathrm{d}t}H(t)\right)\mathrm{d}t = \left(\sum_m Tr\left(H(t)\mathbf{D}_m(t)[\rho(t)]\right)\right)\mathrm{d}t, \tag{3.14}$$

having used the relation $\mathrm{Tr}\left(-i[H(t),\rho]H(t)\right) = 0$.

With these definitions the First Law of Thermodynamics can be written as a differential equation

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \frac{\delta Q}{\mathrm{d}t} - \frac{\delta W}{\mathrm{d}t}. \tag{3.15}$$

Integrating the latter we have

$$\begin{aligned} Q(0,t) &= \int_0^t Tr\left(\frac{\mathrm{d}\rho(s)}{\mathrm{d}s}h_s\right)\mathrm{d}s = \sum_m Q_m(0,t) \\ Q_m(0,t) &\equiv \int_0^t Tr\left(H(s)\mathbf{D}_m(s)[\rho(s)]\right)\mathrm{d}s \end{aligned} \tag{3.16}$$

where $Q_m(0,t)$ represents the heat exchanged with the m-th bath in the time interval $[0,t]$.

3.3. Entropy production and Second Law

3.3.1. Von Neumann entropy

Before stating the Second Law of Thermodynamics in the context of open quantum systems, it is necessary to introduce the Von Neumann entropy of quantum states and some of its properties. We start from the *Shannon entropy* first:

Definition 10. *Shannon entropy.* Consider a classical discrete probability distribution Π: a set of n events with an associated set of probabilities $\Pi = \{p_i\}_{i=1\ldots n}$. The Shannon entropy attributed to such a distribution is

$$H(\Pi) := -\sum_i p_i \log p_i \ \geq 0,$$

where the contribution of each single event is $-p_i \log p_i$ if $p_i \neq 0$ or 0 otherwise, by continuity.

The Shannon entropy is semipositive defined, since all the probabilities p_i are smaller or equal to 1. Also: $H(\Pi) = 0$ if and only if $p_i = 1$ for one i and all the others are zero, while in the maximally random distribution, that is $p_i = 1/n \ \forall i$, we have $H(\Pi) = \log n$.

Definition 11. *Von Neumann entropy.* For a quantum state described by a density matrix ρ, the Von Neumann entropy is defined as

$$S(\varrho) := -\kappa_B \sum_j \lambda_j \log \lambda_j = -\kappa_B \mathrm{Tr}(\rho \log \varrho) \ \geq 0. \tag{3.17}$$

The extreme cases of maximum and minimum entropy correspond respectively to the state $\mathbf{1}/n$ and to any pure state.

Furthermore, the Von Neumann entropy is inviarant under unitary transformations

$$S(U\rho U^\dagger) = S(\rho), \qquad \text{if } U^\dagger U = \mathbf{1}, \tag{3.18}$$

and is sub-additive on bipartite systems $A + B$, which means that

$$S(\rho) \leq S(\rho_A) + S(\rho_B), \tag{3.19}$$

where ρ is a state of the whole system $A + B$ and $\rho_A = \mathrm{Tr}_B\rho$, $\rho_B = \mathrm{Tr}_A\rho$. For a separable state the equality is verified: $S(\rho) = S(\rho_A) + S(\rho_B)$, while for entangled systems this is not true.

3.3.2. Entropy production

Given an open quantum system whose reduced dynamics is assigned by a time-evolution law $t \mapsto \rho(t)$, its entropy is also a function of time

$$S(t) = -\kappa_B \mathrm{Tr}(\rho(t) \log \rho(t)). \tag{3.20}$$

We have seen that, in the classical case, we can distinguish an internal and an external contribution to the entropy variation upon an infinitesimal transformation of the system.

This suggests us to introduce the quantities

$$J_m^S \equiv \frac{1}{T_m}\frac{\delta Q_m(t)}{\mathrm{d}t} = \kappa_B \beta_m \mathrm{Tr}\left(H(t)\mathbf{D}_m(t)[\rho(t)]\right), \qquad \forall m = 1, \ldots, N, \tag{3.21}$$

that we call *quantum entropy flows.* By virtue of eq. (3.5) we have

$$\frac{\mathrm{d}S_{\mathrm{ext}}(t)}{\mathrm{d}t} = \sum_m J_m^S. \tag{3.22}$$

This leads us to the introduction of the *entropy production* as the variation of entropy due to the the internal dynamics of the system:

Definition 12. *Entropy production* of a system in contact with N thermal baths.

$$\sigma(t) \equiv \frac{\mathrm{d}S_{\mathrm{int}}}{\mathrm{d}t} = \frac{\mathrm{d}S(t)}{\mathrm{d}t} - \sum_m J_m^S = -\kappa_B \sum_m \mathrm{Tr}\Big(\mathbf{D}_m(t)[\rho(t)](\log\rho(t) + \beta_m H(t))\Big). \tag{3.23}$$

Notice that the last equality follows from the ciclity of the trace and $\mathrm{Tr}\rho = 1$.

Now, in the situations of physical interest, one may assume that the system has states $\rho_m^{\mathrm{eq}}(t)$ in thermal equlibrium with each bath B_m at each time t: their form is given by the Gibbs expression (3.8). In this case $\beta_m H(t)$ can be written also as $-\log(\mathrm{Tr}(e^{-\beta_m H(t)}) \cdot \rho_m^{\mathrm{eq}}(t))$.

Taking the trace of $\mathbf{D}_m(t)[\rho(t)]\beta_m H(t)$ in (3.23) we have:

$$-\sum_m \mathrm{Tr}\left(\mathbf{D}_m(t)[\rho(t)]\log\left(\mathrm{Tr}(e^{-\beta H_m(t)})\rho_m^{\mathrm{eq}}\right)\right) = -\sum_m \mathrm{Tr}\left(\mathbf{D}_m(t)[\rho(t)]\log\rho_m^{\mathrm{eq}}\right). \tag{3.24}$$

where we have used $\sum_m \mathrm{Tr}(\mathbf{D}_m[\rho(t)]) = 0$ which follows from the assumed trace conservation property of the dynamics.

As a consequence we get the following general expression for the entropy production:

$$\sigma(t) = -\kappa_B \sum_m \mathrm{Tr}\left(\mathbf{D}_m(t)[\rho(t)](\log\rho(t) - \log\rho_m^{\mathrm{eq}}(t))\right). \tag{3.25}$$

We shall now focus upon a system in interaction with one single bath; and consider the internal entropy production

$$\sigma(t) = -\kappa_B \mathrm{Tr}\left(\mathbf{D}(t)[\rho(t)]\left(\log\rho(t) - \log\rho_\beta\right)\right), \qquad \mathbf{D}(t)[\rho_\beta] = 0. \tag{3.26}$$

In order to show the main result of this chapter, we introduce another quantity, that will allow us to express the entropy production as a derivative. This quantity is called *relative entropy* and is defined for every pair of states ρ and ρ'.

Definition 13. *Relative entropy* of $\rho, \rho' \in \mathcal{S}(S)$:

$$S(\rho|\rho') \equiv \kappa_B \mathrm{Tr}\left(\rho(\log\rho - \log\rho')\right). \tag{3.27}$$

The relative entropy can be used as follows. For fixed t, let Λ_s be the semigroup of maps generated by $\mathbf{D}(t)$: $\Lambda_s = e^{s\mathbf{D}(t)}$, $s \geq 0$. Notice that $\Lambda_s[\rho_\beta(t)] = \rho_\beta(t)$. Then, taking the derivative with respect to s at $s = 0$ of

$$S\left(\Lambda_s[\rho(t)]|\Lambda_s[\rho_\beta(t)]\right) = \mathrm{Tr}\left(\Lambda_s[\rho(t)](\log\Lambda_s[\rho(t)] - \log\rho_\beta(t))\right), \tag{3.28}$$

one gets

$$-\frac{\mathrm{d}}{\mathrm{d}s} S\left(\Lambda_s[\rho(t)]|\Lambda_s[\rho_\beta(t)]\right)_{|s=0} = -\mathrm{Tr}\left(\mathbf{D}(t)[\rho(t)](\log\Lambda_s[\rho(t)] - \log\rho_\beta(t)\right) = \sigma(t). \tag{3.29}$$

Indeed, $\mathrm{Tr}\left(\Lambda_s[\rho(t)]\frac{\mathrm{d}}{\mathrm{d}s}\log\Lambda_s[\rho(t)]_{|s=0}\right) = \mathrm{Tr}(\mathbf{D}(t)[\rho(t)]) = 0$.

The last step we need is the so-called *Lindblad H-theorem* for semigroups of completely positive maps [30] which follows from the monotonicity of the relative entropy under completely positive, trace-preserving maps.

Theorem 6. *[30] Given a completely positive trace-preserving map Λ and an invariant state ρ' such that $\Lambda[\rho'] = \rho'$, then*

$$S(\Lambda[\rho]|\Lambda[\rho']) \leq S(\rho|\rho') \qquad \forall \rho, \rho' \in \mathcal{S}(S). \tag{3.30}$$

Since the time-dependent Master Equation

$$\partial_t \rho(t) = -i[H(t), \rho(t)] + \mathbf{D}(t)[\rho(t)] \tag{3.31}$$

is assumed to be of the Kossakowski-Lindblad type, the time-evolution considered here is such that $\{\Lambda_s\}_{s\geq 0}$, $\Lambda_s = e^{s\mathbf{D}(t)}$, is a semigroup of completely positive, trace-preserving maps for any fixed $t \geq 0$.

Thus, using this theorem, one concludes that the entropy production in the class of quantum systems we are dealing with is always non-negative at any time $t \geq 0$:

$$\sigma(t) = -\kappa_B \mathrm{Tr}\left(\mathbf{D}(t)\rho(t)(\log\rho(t) - \log\rho_\beta(t))\right) \geq 0. \tag{3.32}$$

This result easily extends to more than one bath.

We summarize here the conditions we require for this result to be true. For every bath B_m:

- $\mathbf{D}_m(t)$ is slowly varying in t with respect to the m-th reservoir relaxation time;

- $\rho_m^{\mathrm{eq}}(t)$ is a Gibbs thermal state such that $\mathbf{D}_m(t)[\rho_m^{\mathrm{eq}}(t)] = 0$ at each fixed t: this is necessary for writing the entropy production $\sigma(t)$ in terms of the relative entropy;
- $\mathbf{D}_m(t)$ generates a completely positive dynamics: sufficient for ensuring a non-negative internal entropy production.

These requirements may seem rather restrictive, especially the assumption that the system admits a stationary state in the Gibbs form for every bath B_m, nevertheless the definition of entropy production can be generalized to the case of a generic time-evolution described by a semigroup of completely positive maps, as follows [**spohn˙entropy˙2008**]:

Definition 14. *Entropy production.* Let $\{\Lambda_t\}_{t\geq 0}$ be a semigroup of completely positive dynamical maps $\Lambda_t = e^{t\mathbf{L}}$, and let ρ_{st} be a state invariant for Λ_t, i.e. $\Lambda_t[\rho_{\mathrm{st}}] = 0$, for all $t \geq 0$. Then the entropy production σ in the state $\rho_t = \Lambda_t[\rho]$ relative to ρ_{st} is defined by

$$\sigma(\rho_t) \equiv -\frac{\mathrm{d}}{\mathrm{d}t} S(\Lambda_t[\rho]|\rho_{\mathrm{st}}) = -\mathrm{Tr}\left(\mathbf{L}[\rho_t](\log\rho_t - \log\rho_{\mathrm{st}})\right), \tag{3.33}$$

whenever the derivative exists.

In the latter definition there is no explicit time-dependence in the generator $\mathbf{L}$ of the reduced dynamics, so that we have a Markovian one-parameter semigroup. It has been shown [**spohn˙entropy˙2008**] that

- $\sigma \equiv 0$ if and only if the generator of the dynamics is purely Hamiltonian: $\mathbf{L} \equiv 0$;
- σ is convex: if ρ_1 and ρ_2 are two states of the system, and $\lambda_1, \lambda_2 \geq 0$, $\lambda_1 + \lambda_2 = 1$, then

$$\sigma(\lambda_1\rho_1) + \sigma(\lambda_2\rho_2) \geq \sigma(\lambda_1\rho_1 + \lambda_2\rho_2). \tag{3.34}$$

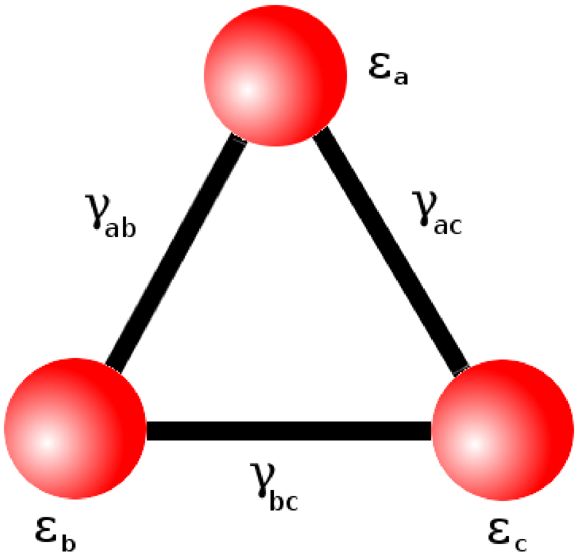
In the end, the non-negativity of the entropy production for a completely positive dynamics, as defined by (3.33), is an important result that maintains its validity also in more general situations, where the stationary state is not necessary a thermal Gibbs state. Complete positivity is a sufficient requirement and not a necessary one, nevertheless lack of CP is associated to violations of the Second Law of Thermodynamics, as we will see in the next chapter.

Chapter 4.

A concrete case: current pumping in a minimal ring model

In this chapter we consider a concrete application of the results discussed in the previous chapters; namely, we study from a thermodynamical point of view a specific open quantum system [31]: three electrons can freely move in a minimal three-site circuit, where an external periodical pumping is applied. The setup is such that there exists one degenerate doubly-occupied ground-state, and the overall system dynamics can be reduced to the dynamics of a pseudospin (or "qubit") under the action of a periodic Hamiltonian. Furthermore, the influence of a noisy environment has a dissipative effect which eventually produces the establishing of a steady DC current in a regime condition. The dependence of the steady current on the driving frequency is the key point of the original paper; since this observable turns out to be proportional to the pseudospin polarization at large times, its final value is directly related to the asymptotic state of the system.

4.1. The model



The minimal circuit ring is constituted by three identical sites a, b, c, each characterized by an electronic level whose energy is cyclically modulated according to the law $\epsilon_i(t) = -\hbar\Delta\cos(\Omega t + \phi_i)$ $(i = a, b, c)$, with phases $\phi_a = 0$, $\phi_b = -2\pi/3$, $\phi_c = 2\pi/3$. Δ is the amplitude of the applied potential, and Ω the frequency. Every couple of sites (i, j) is separated by an energy hopping γ_{ij}. In the scheme considered in [31] all these hoppings are identical: $\gamma_{ij} = \gamma_0$ $(i, j = 1, 2, 3)$, hence the net current inside the circuit is generated by the external pumping.

The Hamiltonian can be expressed with respect to the orthonormal basis of orbitals $|a\rangle$, $|b\rangle$, $|c\rangle$:

$$\begin{pmatrix} \epsilon_a(t) & -\gamma_0 & -\gamma_0 \\ -\gamma_0 & \epsilon_b(t) & -\gamma_0 \\ -\gamma_0 & -\gamma_0 & \epsilon_c(t) \end{pmatrix}, \tag{4.1}$$

The bare Hamiltonian without the application of any external bias is

$$H_0 = \begin{pmatrix} 0 & -\gamma_0 & -\gamma_0 \\ -\gamma_0 & 0 & -\gamma_0 \\ -\gamma_0 & -\gamma_0 & 0 \end{pmatrix}. \tag{4.2}$$

The spectrum of this Hamiltonian is $\{-2\gamma_0, \gamma_0\}$, where $-2\gamma_0$ is the energy of the ground state

$$|0\rangle = \frac{|a\rangle + |b\rangle + |c\rangle}{\sqrt{3}}, \tag{4.3}$$

and γ_0 is the 2-degenerated energy level with eigenstates

$$\begin{aligned} |x\rangle &= \frac{|b\rangle - |c\rangle}{\sqrt{2}}; \\ |y\rangle &= \frac{2\,|a\rangle - |b\rangle - |c\rangle}{\sqrt{6}}. \end{aligned} \tag{4.4}$$

In the lowest energy configuration and in the hypothesis that electron-electron interactions are negligible when compared to the energy hoppings γ_0, two electrons occupy the ground state $|0\rangle$ while the third is in a state living in the subspace spanned by the excited doublet $\{|x\rangle, |y\rangle\}$. When the periodic potential is switched on, H_0 is incremented by a perturbing Hamiltonian given by the diagonal matrix $\mathrm{Diag}(\epsilon_a(t), \epsilon_b(t), \epsilon_c(t))$, which can be rewritten in the basis $\{|0\rangle, |x\rangle, |y\rangle\}$ as

$$H_{\text{bias}}(t) = \begin{pmatrix} 0 & \frac{\epsilon_b(t)-\epsilon_c(t)}{\sqrt{6}} & \frac{\epsilon_a(t)}{\sqrt{2}} \\ \frac{\epsilon_b(t)-\epsilon_c(t)}{\sqrt{6}} & -\frac{\epsilon_a(t)}{2} & \frac{\epsilon_c(t)-\epsilon_b(t)}{2\sqrt{3}} \\ \frac{\epsilon_a(t)}{\sqrt{2}} & \frac{\epsilon_c(t)-\epsilon_b(t)}{2\sqrt{3}} & \frac{\epsilon_a(t)}{2} \end{pmatrix}. \tag{4.5}$$

As long as the applied bias is a small perturbation of the bare Hamiltonian H_0, namely if the energy gap $\gamma_0 - (-2\gamma_0) = 3\gamma_0$ between the ground state and the excited doublet is much greater than the pumped energies $|\epsilon_i(t)|$, we can exclude transitions between $|0\rangle$ and the subspace spanned by $\{|x\rangle, |y\rangle\}$; consequently we can still assume that the ground state remains occupied by two electrons and the dynamics of the system is determined by the third electron, whose state vector is a qubit in the 2-dimensional subspace $\{|x\rangle, |y\rangle\}$.

The evolution of this pseudospin system is therefore described by the Hamiltonian

$$H_S(t) = -\frac{1}{2\sqrt{3}} \begin{pmatrix} \sqrt{3}\epsilon_a(t) & \epsilon_b(t) - \epsilon_c(t) \\ \epsilon_b(t) - \epsilon_c(t) & -\sqrt{3}\epsilon_a(t) \end{pmatrix}. \tag{4.6}$$

Substituting the periodic potentials

$$\begin{cases} \epsilon_a(t) = -\hbar\Delta \cos \Omega t \\ \epsilon_b(t) = -\hbar\Delta \cos(\Omega t - 2\pi/3) \\ \epsilon_c(t) = -\hbar\Delta \cos(\Omega t + 2\pi/3), \end{cases} \tag{4.7}$$

into (4.6), we have finally

$$H_S(t) = \frac{\hbar\Delta}{2}(\cos(\Omega t)\sigma^z + \sin(\Omega t)\sigma^x), \tag{4.8}$$

written in terms of the Pauli matrices.

In order to be consistent with the notation used in the preceding chapters, in the following we will use the natural units: $\hbar = 1$.

To introduce the dissipative effect of the environment the latter is modeled as an ensemble of non-interacting harmonic oscillators in thermal equilibrium at temperature T. Since the system has only two modes, we can assume the oscillators to be bidimensional. Therefore the Hamiltonian H_E for the thermal bath must have the form

$$H_E = \sum_{\xi=z,x} \sum_{\nu} \left(\frac{p_{\xi,\nu}^2}{2m} + \frac{m\omega_\nu^2 q_{\xi,\nu}^2}{2} \right), \tag{4.9}$$

where ω_ν is the frequency of the ν-th oscillator, $q_{\xi,\nu}$ are the oscillators position observables and $p_{\xi,\nu}$ their conjugate variables (the momenta).

The coupling betweem the system modes and the thermal bath is determined by the interaction Hamiltonian

$$H_{SE} = \sum_{\xi=z,x} \sum_{\nu} \sqrt{2m\omega_\nu}\lambda_{\xi,\nu}\sigma^\xi \otimes q_{\xi,\nu}. \tag{4.10}$$

$\lambda_{\xi,\nu}$ are the coupling constants (in principle depending also on the specific mode, but we will assume $\lambda_{\xi,\nu} \equiv \lambda_\nu$).

We see that H_{SE} is formally analogous to the $\lambda H'$ interaction Hamiltonian introduced in (2.53), the only difference being the use of many coupling constant instead of one, which is irrelevant since we are interested in the limit $\lambda_{\xi.\nu} \to 0$; thus we can always redefine the operators in order to have a single λ going to zero.

Hence the global Hamiltonian of the system is given by $H_S(t) + H_{SE} + H_E$.

The aim of the original article is to determine the steady asymptotic DC current flowing in the circuit and its dependence on the applied frequency Ω.

In our pseudospin representation the current $I(t)$ generated by the free electron inside the circuit is proportional to the expectation value of σ^y[1]

$$I(t) = I_0 \langle \sigma^y \rangle_{\psi(t)}, \tag{4.11}$$

[1]See Appendix A.4

where $|\psi(t)\rangle$ is the state at time t and I_0 given by

$$I_0 = \frac{e\gamma_0}{\sqrt{3}} \qquad e = \text{elementary charge.} \tag{4.12}$$

With the introduction of the unitary transformation

$$R_y(\Omega t) = e^{-i\frac{\Omega t}{2}\sigma^y}, \tag{4.13}$$

geometrically corresponding to a rotation about the y axis, one can perform a change of reference frame, by mapping every state $|\psi_S(t)\rangle$ of the system to a state $|\tilde{\psi}_S(t)\rangle$ given by:

$$|\tilde{\psi}_S(t)\rangle \equiv R_y^{-1}(\Omega t)\,|\psi_S(t)\rangle\,. \tag{4.14}$$

It follows that $H_S(t)$ can be rewritten as

$$H_S(t) = \frac{\Delta}{2} R_y(\Omega t)\sigma^z R_y^{-1}(\Omega y). \tag{4.15}$$

In this rotating reference frame, the Schrödinger equation for $|\tilde{\psi}_S(t)\rangle$ reads

$$\begin{aligned}
i\partial_t|\tilde{\psi}_S(t)\rangle &= i\left(i\frac{\Omega}{2}\sigma^y R_y^{-1}(\Omega t)\right)|\psi_S(t)\rangle + iR_y^{-1}(\Omega t)\partial_t\,|\psi_S(t)\rangle = \\
&= -\frac{\Omega}{2}\sigma^y|\tilde{\psi}_S(t)\rangle + R_y^{-1}(\Omega t)H_S(t)R_y(\Omega t)|\tilde{\psi}_S(t)\rangle = \\
&= -\frac{\Omega}{2}\sigma^y|\tilde{\psi}_S(t)\rangle + R_y^{-1}(\Omega t)\left(\frac{\Delta}{2}R_y(\Omega t)\sigma^z R_y^{-1}(\Omega t)\right)R_y(\Omega t)|\tilde{\psi}_S(t)\rangle = \\
&= \left(-\frac{\Omega}{2}\sigma^y + \frac{\Delta}{2}\sigma^z\right)|\tilde{\psi}_S(t)\rangle = H_{\text{eff}}|\tilde{\psi}_S(t)\rangle,
\end{aligned} \tag{4.16}$$

with a new, time-independent Hamiltonian

$$H_{\text{eff}} = \frac{\Delta}{2}\sigma^z - \frac{\Omega}{2}\sigma^y = \frac{\omega'}{2}\hat{\boldsymbol{n}}\cdot\boldsymbol{\sigma}, \tag{4.17}$$

with frequency

$$\omega' = \sqrt{\Omega^2 + \Delta^2}, \tag{4.18}$$

and unit vector

$$\hat{n} = \left(0, -\frac{\Omega}{\omega'}, \frac{\Delta}{\omega'}\right). \tag{4.19}$$

Thus, if we consider just the isolated micro-circuit, the time-evolution in the corresponding qubit description consists in a Larmor precession around the $\hat{n}$-axis with frequency ω'.

Since $R_y(\Omega t)$ commutes with σ^y, the current supported by the microcircuit at time t can be computed as

$$I(t) = I_0 \langle \tilde{\psi}_S(t) | \sigma^y | \tilde{\psi}_S(t) \rangle. \tag{4.20}$$

It is convenient to make a change of basis from $\sigma^x, \sigma^y, \sigma^z$ to a new Pauli triple $\hat{\sigma}^x, \hat{\sigma}^m, \hat{\sigma}^n$:

$$\begin{cases} \hat{\sigma}^x = \sigma^x \\ \hat{\sigma}^m = \dfrac{\Delta}{\omega'} \sigma^y + \dfrac{\Omega}{\omega'} \sigma^z \\ \hat{\sigma}^n = -\dfrac{\Omega}{\omega'} \sigma^y + \dfrac{\Delta}{\omega'} \sigma^z \end{cases}. \tag{4.21}$$

The inverse transformation for σ^y gives:

$$\sigma^y = \frac{\Delta}{\omega'} \hat{\sigma}^m - \frac{\Omega}{\omega'} \hat{\sigma}^n. \tag{4.22}$$

We can write $\hat{\sigma}^m$ in terms of the ladder operators for the $\hat{\sigma}^n$ eigenstates:

$$\begin{cases} \hat{\sigma}^n_+ \, |\hat{n}, +\rangle = 0 \\ \hat{\sigma}^n_+ \, |\hat{n}, -\rangle = |\hat{n}, +\rangle \\ \hat{\sigma}^n_- \, |\hat{n}, +\rangle = |\hat{n}, -\rangle \\ \hat{\sigma}^n_- \, |\hat{n}, -\rangle = 0 \end{cases}, \tag{4.23}$$

with $\hat{\sigma}^n_\pm = \frac{1}{2} \left(\hat{\sigma}^x \pm i \hat{\sigma}^m \right)$.

Consequently

$$\hat{\sigma}^m = \frac{1}{i} \left(\hat{\sigma}^n_+ - \hat{\sigma}^n_- \right). \tag{4.24}$$

Therefore, if the initial state is one of the two $\hat{\sigma}^n$ eigenstates, $|\hat{n}, +\rangle$ or $|\hat{n}, -\rangle$, the system does not evolve and the current I is a steady DC current given by $\mp I_0 \frac{\Omega}{\omega'}$, respectively. Indeed, the expression (4.20) of the current yields

$$\begin{aligned} I(t) &= I_0 \frac{\Delta}{\omega'} \langle \hat{n}, \pm \,|\, \hat{\sigma}^m \,|\, \hat{n}, \pm \rangle - I_0 \frac{\Omega}{\omega'} \langle \hat{n}, \pm \,|\, \hat{\sigma}^n \,|\, \hat{n}, \pm \rangle = \\ &= \mp I_0 \frac{\Omega}{\omega'}. \end{aligned} \tag{4.25}$$

Any other initial condition gives rise to an AC current in addition to the DC, due to the Larmor precession of the ket $|\tilde{\psi}_S(t)\rangle$, and the DC current is determined by the projection of this state on the eigenstates of $H_{\text{eff}} = \omega'\hat{\sigma}^n/2$: $|\hat{n}, \pm\rangle$.

In the density matrix formalism the system state is characterized by a matrix $\tilde{\rho}_S$ that will be conveniently expanded in the basis $\{\hat{\sigma}^x, \hat{\sigma}^m, \hat{\sigma}^n\}$, giving the Bloch representation

$$\tilde{\rho}_S = \frac{1}{2}(\mathbf{1} + a\hat{\sigma}^x + b\hat{\sigma}^m + c\hat{\sigma}^n), \tag{4.26}$$

where $(1, a, b, c)$ is the so-called Bloch vector associated with $\tilde{\rho}_S$. Since the time-evolution law now reads equation:

$$\partial_t\tilde{\rho}_S = -i\frac{\omega'}{2}[\hat{\sigma}^n, \tilde{\rho}_S], \tag{4.27}$$

the net DC contribution to the current $I(t)$ – that is the observable in which we are interested – is determined by the third component of the Bloch vector of $\tilde{\rho}_S$, c, the only component that does not change in time under (4.27).

Denoting by P

$$P = -\text{Tr}(\hat{\sigma}^n\tilde{\rho}_S), \tag{4.28}$$

the opposite of c, then the DC current sustained by the microcircuit becomes

$$I = I_0 P\frac{\Omega}{\omega'}. \tag{4.29}$$

In passing to the rotating reference frame in the global Hamiltonian $H = H_S(t) + H_E + H_{SE}$ the system's observables change as follows:

$$\tilde{\sigma}^\xi(t) = R_y^{-1}(\Omega t)\sigma^\xi R_y(\Omega t). \tag{4.30}$$

Consequently H_{SE} changes into a time-dependent interaction term:

$$\tilde{H}_{SE}(t) = \sum_{\xi=z,x}\sum_\nu \sqrt{2m\omega_\nu}\tilde{\sigma}^\xi(t) \otimes q_{\xi,\nu}, \tag{4.31}$$

while H_E of course remains unchanged.

The total Hamiltonian in the rotating reference frame thus becomes

$$\tilde{H}_T(t) = H_{\text{eff}} + \tilde{H}_{SE}(t) + \tilde{H}_E, \tag{4.32}$$

where H_{eff} stands for $H_{\text{eff}} \otimes \mathbf{1}_E$ and $\tilde{H}_E$ for $\mathbf{1}_S \otimes \tilde{H}_E$.

With this transformation we have obtained an Hamiltonian whose explicit time dependence is transferred from the system Hamiltonian to the interaction term $\tilde{H}_{SE}$.

4.2. Master Equation and stationary state

While the microcircuit is represented as a two-level (qubit) system, the environment is described by a many-body system; though the number of its degrees of freedom is taken to be infinite, we shall stick to its states being represented by

We assume that at time $t = 0$ the system and the environment are uncorrelated:

$$\tilde{\rho}_{S+E}(0) = \tilde{\rho}_S(0) \otimes \rho_E, \tag{4.33}$$

where is ρ_E a given equilibrium state of the environment and $\tilde{\rho}_S(t)$ the density matrix for the system.

The Liouville-Von Neumann equation is

$$\partial_t \tilde{\rho}_{S+E} = \tilde{\mathbf{L}}_{S+E}(t)[\tilde{\rho}_{S+E}], \tag{4.34}$$

with

$$\begin{aligned} \tilde{\mathbf{L}}_{S+E}(t)[\cdot] &= -i[H_{\text{eff}}\,,\,\cdot] - i[\tilde{H}_E\,,\,\cdot] - i[\tilde{H}_{SE}(t)\,,\,] = & (4.35)\\ &= \tilde{\mathbf{L}}_S[\cdot] + \tilde{\mathbf{L}}_E[\cdot] + \tilde{\mathbf{L}}_{SE}[\cdot]. & (4.36) \end{aligned}$$

We are seeking an expression of the Master Equation for the reduced dynamics of the form:

$$\partial_t \tilde{\rho}_S(t) = -i[H_{\text{eff}},\, \tilde{\rho}_S(t)] + \mathbf{K}[\tilde{\rho}_S(t)]. \tag{4.37}$$

In Appendix A.5 we derive in full details the Master Equation, following the procedure sketched in Appendix A.1, obtaining the following result

$$\begin{aligned} \partial_t \tilde{\rho}_S(t) = -i[H_{\text{eff}},\, \tilde{\rho}_S(t)] - \sum_{\xi=z,x} \int_0^{+\infty} \mathrm{d}w \Big\{ G_\xi(w) \Big[e^{-w\tilde{\mathbf{L}}_S} \tilde{\sigma}^\xi(w+t),\, \tilde{\sigma}^\xi(t)\tilde{\rho}_S(t) \Big] + \\ + G^*_\xi(w) \Big[\tilde{\rho}_S(t)\tilde{\sigma}^\xi(t),\, e^{-w\tilde{\mathbf{L}}_S}\tilde{\sigma}^\xi(w+t) \Big] \Big\}, \end{aligned} \tag{4.38}$$

where we have introduced the functions $G_\xi(w)$, which are the time correlators calculated tracing over the bath degrees of freedom

$$G_\xi(w) \equiv \int_0^{+\infty} \mathrm{d}k\, J_\xi(k) \left(\cos kw \coth \frac{\beta k}{2} - i \sin kw \right). \tag{4.39}$$

$\beta = \kappa_B T$ is the Boltzmann factor and $J_\xi(k)$ is the *spectral density*

$$J_\xi(k) \equiv \sum_\mu \lambda^2_{\xi,\mu}\delta(k-\omega_\mu). \tag{4.40}$$

Under the further assumption that spectral density be homogeneous in the modes z, x, $J_z(k) = J_x(k) \equiv J(k)$, in the M.E. the explicit time dependence disappears.

Again, we make a change of basis from $\sigma^x, \sigma^y, \sigma^z$ to

$$\begin{cases} \hat{\sigma}^x = & \sigma^x \\ \hat{\sigma}^m = & \dfrac{\Delta}{\omega'} \quad \sigma^y + \dfrac{\Omega}{\omega'} \quad \sigma^z \\ \hat{\sigma}^n = & -\dfrac{\Omega}{\omega'} \quad \sigma^y + \dfrac{\Delta}{\omega'} \quad \sigma^z \end{cases}. \tag{4.41}$$

or, in compact form,

$$\sigma^\eta = \sum_{\tau=x,m,n} \Lambda_{\eta\tau}\hat{\sigma}^\tau, \qquad \Lambda = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \frac{\Delta}{\omega'} & -\frac{\Omega}{\omega'} \\ 0 & \frac{\Omega}{\omega'} & \frac{\Delta}{\omega'}. \end{pmatrix} \tag{4.42}$$

Since we have performed an orthogonal rotation, the new basis keeps the commutation rules of the original Pauli matrices, once we substitute $(\sigma^x, \sigma^y, \sigma^x) \mapsto (\sigma^x, \sigma^m, \sigma^n)$.

We can also write the rotated system observables $\tilde{\sigma}^\xi$ (4.30) as linear combinations of the x, y, z Pauli matrices:

$$\tilde{\sigma}^\xi(t) = R_y^{-1}(\Omega t)\sigma^\xi R_y(\Omega t) = \sum_{\eta=x,y,z} R(\Omega t)_{\xi\eta}\sigma^\eta, \tag{4.43}$$

with

$$R(\Omega t) = \begin{pmatrix} \cos\Omega t & 0 & \sin\Omega t \\ 0 & 1 & 0 \\ -\sin\Omega t & 0 & \cos\Omega t \end{pmatrix}, \tag{4.44}$$

Then we can write $\tilde{\sigma}^\xi(t)$ in terms of $(\hat{\sigma}^x, \hat{\sigma}^m, \hat{\sigma}^n)$

$$\tilde{\sigma}^\xi(t) = \sum_{\eta=x,y,z}\sum_{\tau=x,m,n} R(\Omega t)_{\xi\eta}\Lambda_{\eta\tau}\hat{\sigma}^\tau \tag{4.45}$$

and consequently the expression $e^{-w\tilde{\mathbb{L}}_S}\tilde{\sigma}^\xi(w+t)$ becomes

$$e^{-w\tilde{\mathbb{L}}_S}\tilde{\sigma}^\xi(w+t) = \sum_{\chi=x,y,z}\ \sum_{\mu,\lambda\in\{x,m,n\}} R(\Omega(w+t))_{\xi\chi}\Lambda_{\chi\mu}Q(-w\omega')_{\mu\lambda}\hat{\sigma}^\lambda, \tag{4.46}$$

where the matrix $Q(-w\omega')$

$$Q(-w\omega') = \begin{pmatrix} \cos\omega' w & -\sin\omega' w & 0 \\ \sin\omega' w & \cos\omega' w & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{4.47}$$

performs a rotation about the $\hat{n}$-axis, corresponding to the action of the effective Hamiltonian H_{eff} (4.17)

$$e^{iw\omega'\hat{\sigma}^n/2}\hat{\sigma}^x e^{-iw\omega'\hat{\sigma}^n/2} = \cos w\omega'\hat{\sigma}^x - \sin w\omega'\hat{\sigma}^m \tag{4.48}$$

$$e^{iw\omega'\hat{\sigma}^n/2}\hat{\sigma}^m e^{-iw\omega'\hat{\sigma}^n/2} = \sin w\omega'\hat{\sigma}^x + \cos w\omega'\hat{\sigma}^m. \tag{4.49}$$

Substituting (4.45) and (4.46) into the first commutator of eq. (4.38) we have [2]

$$\left[\tilde{\rho}_S\tilde{\sigma}^\xi(t), e^{-w\tilde{\mathbb{L}}_S}\tilde{\sigma}^\xi(t+w)\right] =$$

$$= \sum_{\eta,\chi=x,y,z}\ \sum_{\tau,\mu,\lambda=x,m,n} \Lambda^{-1}_{\tau\eta}\underline{\left(\sum_{\xi=x,z} R(-\Omega t)_{\eta\xi}R(\Omega(t+w))_{\xi\chi}\right)}\Lambda_{\chi\mu}Q(-w\omega')_{\mu\lambda}\left[\tilde{\rho}_S(t)\sigma^\tau, \sigma^\lambda\right], \tag{4.50}$$

we find that the explicit time dependence of this expression disappears: the underlined expression in the previous equation is worked out in A.6 and gives $\tilde{R}(\Omega w)_{\eta\chi}$, where the matrix $\tilde{R}(\Omega w)$ is

$$\tilde{R}(\Omega w) \equiv \begin{pmatrix} \cos\Omega w & 0 & \sin\Omega w \\ 0 & 0 & 0 \\ -\sin\Omega w & 0 & \cos\Omega w \end{pmatrix}. \tag{4.51}$$

The second commutator is just the hermitian conjugate of the first.

[2] in the following we will omit the hat ˆ over the sigmas

Further developing the matricial expressions we arrive at the following compact form of the operator $\mathbf{K}$ (see Appendix A.7):

$$\mathbf{K}[\tilde{\rho}_S] = -\sum_{\tau,\lambda\in\{x,m,n\}} \left(A(\Omega,\omega')_{\tau\lambda} \left[\tilde{\rho}_S\sigma^\tau, \sigma^\lambda\right] + A(\Omega,\omega')^*_{\tau\lambda}[\sigma^\lambda, \sigma^\tau\tilde{\rho}_S] \right) \tag{4.52}$$

$$= \sum_{\tau,\lambda\in\{x,m,n\}} C(\Omega,\omega')_{\tau\lambda} \left(\sigma^\lambda\tilde{\rho}_S\sigma^\tau - \frac{1}{2}\left\{\sigma^\tau\sigma^\lambda, \tilde{\rho}_S\right\} \right) - i[H^{(1)}, \tilde{\rho}_S] = \tag{4.53}$$

$$= \mathbf{D}[\tilde{\rho}_S] - i[H^{(1)}, \tilde{\rho}_S], \tag{4.54}$$

where

$$C(\Omega,\omega')_{\tau,\lambda} = A(\Omega,\omega')_{\tau\lambda} + A(\Omega,\omega')^*_{\lambda\tau}, \tag{4.55}$$

$$H^{(1)} = \frac{i}{2} \sum_{\tau,\lambda\in\{x,m,n\}} \left(A(\Omega,\omega')_{\tau\lambda} - A(\Omega,\omega')^*_{\lambda\tau} \right) \sigma^\tau\sigma^\lambda, \tag{4.56}$$

$$A(\Omega,\omega') = \int_0^{+\infty} \mathrm{d}w\, \Lambda^{-1}\tilde{R}(\Omega w)\Lambda Q(-\omega' w) G(w)^*. \tag{4.57}$$

From eq. (4.52) we have immediately the Kossakowski-Lindblad version of the Master Equation, where the purely dissipative part has been separated from the anti-hermitian generator $-i[H^{(1)}, \cdot]$, which is hidden into the double commutator form (4.38), and corresponds to the action of a correction Hamiltonian $H^{(1)}$, often called "*Lamb shift*" Hamiltonian. The Lamb-shift correction is a λ^2 order contribution to the effective Hamiltonian, as it can be easily observed noting that the time correlator $G(w)$, containing the $\lambda^2_{\xi,\nu}$ coupling constants, appears in the expression of $H^{(1)}$ through $A(\Omega,\omega')$.

4.3. Asymptotic current in the weak coupling limit

In order to determine the DC current $I(t)$ (4.29) we need to study the evolution of the system state $\tilde{\rho}_S(t)$. We have already seen that, in absence of external perturbations, there exist two opposite steady current $\mp I_0\frac{\Omega}{\omega'}$ corresponding to the eigenstates $|\hat{n},\pm\rangle$ of the effective Hamiltonian H_{eff}: this means that if the system starts from an initial state $\tilde{\rho}_S(0)$ polarized along $\hat{n}$

$$\tilde{\rho}_S(0) = \frac{1}{2}(\mathbf{1} + c\hat{\sigma}^n),$$

then it remains in that stationary state, producing a DC current. What happens if the initial state is generic and we switch on the interaction with the thermal bath? We will see that even if we start from a non-stationary state, the dissipation will eventually lead the system to an asymptotic state.

First of all we need to reconsider the Master Equation in the light of the considerations in section 2.4.1. On the basis of the integral form of (A.68), we can recognize the same structure of (2.61). This means that the Master Equation corresponds to the generator of type $\mathbf{K}_2$:

$$\partial_t \rho_S = -i[H_{\text{eff}},\, \rho_S] + \lambda^2 \int_0^{+\infty} \mathrm{d}v\, e^{-v\mathbf{L}_S} \mathrm{Tr}_{\mathrm{E}}\big(\mathbf{L}' \circ e^{v(\mathbf{L}_S+\mathbf{L}_E)} \circ \mathbf{L}'[\rho_S \otimes \rho_E]\big), \tag{4.58}$$

that is of Redfield type. As already observed, these kind of equations are in general neither completely positive nor positive. In order to get a physically consistent Master Equation, as indicated in section 2.4.1, one need to perform the so called *rotating wave approximation.* Concretely, following the Davies's prescription we will replace the operator $\mathbf{K}_2$ with its ergodic average

$$\mathbf{K}_3[\tilde{\rho}_S] \equiv \lim_{T\to\infty} \frac{1}{2T} \int_{-T}^{+T} \mathrm{d}\tau \, \left(e^{-\tau\tilde{\mathbf{L}}_S} \circ \mathbf{K}_2 \circ e^{\tau\tilde{\mathbf{L}}_S}\right) [\tilde{\rho}_S]. \tag{4.59}$$

This will guarantee both the completely positive requirement and the convergence of the approximate solution $\tilde{\rho}_S(t)$ to the real evolution, in the limit $\lambda \to 0$, i.e. for arbitrary small couplings.

It is convenient to rewrite the M.E. in the Bloch representation. The Hamiltonian part becomes

$$\begin{aligned} -i[H_{\text{eff}}, \tilde{\rho}_S] &= -i\left[\frac{\omega'}{2}\sigma^n, \tilde{\rho}_S\right] = -\frac{i\omega'}{2}\left[\sigma^n, \frac{a\sigma^x + b\sigma^m}{2}\right] = \frac{\omega'}{2}\left(a\sigma^m - b\sigma^x\right) \\ \text{(in Bloch representation)} \quad &= -2\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{\omega'}{4} & 0 \\ 0 & -\frac{\omega'}{4} & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ a \\ b \\ c \end{pmatrix} \equiv -2\mathcal{H}_{\text{eff}} \left|\tilde{\rho}_S\right\rangle . \end{aligned} \tag{4.60}$$

Consequently, we can write $e^{-\tau\tilde{\mathbf{L}}_S}$ in Bloch representation as

$$e^{2\tau\mathcal{H}_{\text{eff}}} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos\frac{\omega'\tau}{2} & \sin\frac{\omega'\tau}{2} & 0 \\ 0 & -\sin\frac{\omega'\tau}{2} & \cos\frac{\omega'\tau}{2} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} . \tag{4.61}$$

Next, we need to perform the ergodic average in (4.59) with the choice of an *ohmic* spectral density made in [31]:

$$J(k) = \alpha k e^{-\frac{k}{k_c}}. \tag{4.62}$$

With this choice, once we have worked out the term $\mathbf{K}_2$ (4.52), evaluated the integrals in dw and written it in Bloch notation, we can make the ergodic average and we get a matrix of the kind:

$$\begin{aligned}\tilde{\mathcal{K}} \equiv \mathcal{K}_3 \equiv \lim_{T\to\infty} \frac{1}{2T} \int_{-T}^{+T} \mathrm{d}\tau \, e^{2\tau\mathcal{H}_{\mathrm{eff}}} \circ \mathcal{K}_2 \circ e^{-2\tau\mathcal{H}_{\mathrm{eff}}} = \\ = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \mathcal{K}_{2(11)} + \mathcal{K}_{2(22)} & -\mathcal{K}_{2(21)} + \mathcal{K}_{2(12)} & 0 \\ 0 & \mathcal{K}_{2(21)} - \mathcal{K}_{2(12)} & \mathcal{K}_{2(11)} + \mathcal{K}_{2(22)} & 0 \\ \mathcal{K}_{2(30)} & 0 & 0 & \mathcal{K}_{2(33)} \end{pmatrix},\end{aligned} \tag{4.63}$$

where $\mathcal{K}_{2(ij)}$ is the (i,j) component of the 4×4 matrix $\mathcal{K}_2$, representing the operator $\mathbf{K}_2$ in Bloch form.

The complete M.E. in Bloch representation

$$\partial_t \left|\tilde{\rho}_S\right\rangle = -2(\mathcal{H}_{\mathrm{eff}} + \tilde{\mathcal{K}}) \left|\rho\right\rangle, \tag{4.64}$$

admits a stationary state $\hat{\rho} = \frac{1}{2}(\mathbf{1} - \frac{\tilde{\mathcal{K}}_{30}}{\tilde{\mathcal{K}}_{33}}\sigma^n)$:

$$\hat{\rho} = \frac{1}{2}\mathbf{1} - \frac{1}{2}\left(\frac{\Im g_{cs} - 2\frac{\Omega}{\omega'}\Im g_{sc} + \frac{\Omega^2}{\omega'^2}\Im g_{cs}}{\Re g_{cc} + \frac{2\Omega}{\omega'}\Re g_{ss} + \frac{\Omega^2}{\omega'^2}\Re g_{cc}}\right)\sigma^n, \tag{4.65}$$

where we have defined the quantities g_{cs}, g_{sc}, g_{cc}, g_{ss}:

$$\begin{cases} g_{cs} = \displaystyle\int_0^\infty \mathrm{d}w \, G(w) \cos(-\Omega w) \sin(-\omega' w) \\ g_{sc} = \displaystyle\int_0^\infty \mathrm{d}w \, G(w) \sin(-\Omega w) \cos(-\omega' w) \\ g_{ss} = \displaystyle\int_0^\infty \mathrm{d}w \, G(w) \sin(-\Omega w) \sin(-\omega' w) \\ g_{cc} = \displaystyle\int_0^\infty \mathrm{d}w \, G(w) \cos(-\Omega w) \cos(-\omega' w) \end{cases} \tag{4.66}$$

arising from the calculation of the bath time-correlators.

The factors in which we are interested are, after performing the integration:

$$\begin{cases} \Im g_{cs} = \frac{\pi\alpha}{4}\left((\omega'+\Omega)e^{-\frac{\Omega+\omega'}{\omega_c}} + (\omega'-\Omega)e^{-\frac{\omega'-\Omega}{\omega_c}}\right) \\ \Im g_{sc} = \frac{\pi\alpha}{4}\left((\omega'+\Omega)e^{-\frac{\Omega+\omega'}{\omega_c}} - (\omega'-\Omega)e^{-\frac{\omega'-\Omega}{\omega_c}}\right) \end{cases} \tag{4.67}$$

$$\begin{cases} \Re g_{cc} = \frac{\pi\alpha}{4}\left((\omega'+\Omega)e^{-\frac{\Omega+\omega'}{\omega_c}} \coth\left(\frac{\beta(\omega'+\Omega)}{2}\right) + (\omega'-\Omega)e^{-\frac{\Omega-\omega'}{\omega_c}} \coth\left(\frac{\beta(\omega'-\Omega)}{2}\right)\right) \\ \Re g_{ss} = \frac{\pi\alpha}{4}\left((\omega'+\Omega)e^{-\frac{\Omega+\omega'}{\omega_c}} \coth\left(\frac{\beta(\omega'+\Omega)}{2}\right) - (\omega'-\Omega)e^{-\frac{\Omega-\omega'}{\omega_c}} \coth\left(\frac{\beta(\omega'-\Omega)}{2}\right)\right) \end{cases} \tag{4.68}$$

In the end we have found that the system under examination admits a stationary state that is polarized along the $\hat{n}$ axis with a polarization $P = -\mathrm{Tr}(\tilde{\rho}_S \sigma^n)$ given by

$$P = \frac{(\omega'-\Omega)^2 J_+ + (\omega'+\Omega)^2 J_-}{(\omega'-\Omega)^2 c_+ J_+ + (\omega'+\Omega)^2 c_- J_-}, \tag{4.69}$$

where

$$J_\pm \equiv J(\omega' \pm \Omega) = \alpha(\omega' \pm \Omega)e^{-\frac{(\omega'\pm\Omega)}{\omega_c}}, \tag{4.70}$$

$$c_\pm \equiv \coth\left[\frac{\beta(\omega' \pm \Omega)}{2}\right]. \tag{4.71}$$

This polarized state is exactly the same found by [31], the main difference being the fact that, while their result is claimed to be valid only in the limit $\alpha \to 0$ (or $\lambda_\nu^2 \to 0$) and their Master Equation does not admit an exact stationary state, in our treatment the stationary state $\hat{\rho}$ is the real stationary state.

4.4. Complete positivity and positivity

As we have discussed in 2.4.1, any Master Equation derived in a Markovian approximation regime applying the ergodic average, i.e. any Master Equation of the kind (2.67)

$$\partial_t \rho_S(t) = (\mathbf{L}_S + \lambda^2 \mathbf{K}_3)[\rho_S(t)], \tag{4.72}$$

with $\mathbf{K}_3$ given by

$$\mathbf{K}_3[\rho] \equiv \lim_{T\to\infty} \frac{1}{2T} \int_{-T}^{+T} \mathrm{d}t\, e^{-t\mathbf{L}_S} \mathbf{K}_2 e^{t\mathbf{L}_S} \rho, \tag{4.73}$$

ensures that the reduced dynamics is described by a continuous one-parameter semigroup $\{\gamma_t\}_{t\geq 0}$ of maps γ_t that are completeley positive (hence also positive). Consequently our result can be considered free of any physical inconsistency.

On the opposite, we want to show that the dynamics arising from the Master Equation proposed in [31] is not completely positive and, in some cases, is not even positive.

Following a general scheme frequently used in literature [10], they write

$$\frac{\partial \tilde{\rho}_S(t)}{\partial t} = -i[H_{\text{eff}}, \tilde{\rho}_S(t)] - \frac{1}{\hbar^2} \sum_{\xi=z,x} \int_0^\infty d\tau \left\{ G_\xi(\tau) \left[\tilde{\sigma}^\xi(t), U_0^\dagger(-\tau)\tilde{\sigma}^\xi(t-\tau)U_0(-\tau)\tilde{\rho}_S(t) \right] + G_\xi^*(\tau) \left[\tilde{\rho}_S(t)U_0^\dagger(-\tau)\tilde{\sigma}^\xi(t-\tau)U_0(-\tau), \tilde{\sigma}^\xi(t) \right] \right\}, \tag{4.74}$$

where

$$U_0(\tau) = \exp(-iH_{\text{eff}}\tau). \tag{4.75}$$

In appendix A.8 we derive explicitly this Master Equation and we show that it corresponds to the first Markovian approximation discussed in sec. 2.4.1, with a generator of the form

$$\mathbf{L}[\cdot] = -i[H_{\text{eff}}, \cdot] + \lambda^2 \mathbf{K}_1[\cdot]. \tag{4.76}$$

In order to check whether the dynamics generated is completely positive, we recast this equation in Kossakowski-Lindblad form (2.35). We choose as Lindblad operators

$$V_1 \equiv V_{z1} = \frac{1}{\hbar} \int_0^\infty \mathrm{d}\tau\, G(\tau)U_0^\dagger(-\tau)\tilde{\sigma}^z(t-\tau)U_0(-\tau) \tag{4.77a}$$

$$V_2^\dagger \equiv V_{z2}^\dagger = \frac{1}{\hbar}\tilde{\sigma}^z(t) \tag{4.77b}$$

$$V_3 \equiv V_{x1} = \frac{1}{\hbar} \int_0^\infty \mathrm{d}\tau\, G(\tau)U_0^\dagger(-\tau)\tilde{\sigma}^x(t-\tau)U_0(-\tau) \tag{4.77c}$$

$$V_4^\dagger \equiv V_{x2}^\dagger = \frac{1}{\hbar}\tilde{\sigma}^x(t) \tag{4.77d}$$

and the operator $\mathbf{K}$, including with the Lamb shift Hamiltonian $H^{(1)}$, becomes

$$\mathbf{K}[\tilde{\rho}_S] = \sum_{\xi=z,x} \sum_{j,k=1,2} C_{jk} \left(V_{\xi k}\tilde{\rho}_S V_{\xi j}^\dagger - \frac{1}{2}\left\{ V_{\xi j}^\dagger V_{\xi k} \right\} \right) - i[H^{(1)}, \tilde{\rho}_S], \tag{4.78}$$

where the matrix C is

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \tag{4.79}$$

In terms of V_1, V_2, V_3, V_4 eq. (4.78) can be easily rewritten

$$\mathbf{K}[\tilde{\rho}_S] = \sum_{j,k=1}^{4} \tilde{C}_{jk} \left(V_k \tilde{\rho}_S V_j^\dagger - \frac{1}{2}\{V_j^\dagger V_k,\, \tilde{\rho}_S\} \right) - i[H^{(1)},\, \tilde{\rho}_S], \tag{4.80}$$

with the Kossakowski-Lindblad matrix $\tilde{C}$

$$\tilde{C} = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \tag{4.81}$$

which is clearly non-positive definite. By virtue of the Gorini-Kossakowski-Sudarshan-Lindblad theorem, the generated dynamics is not completely positive.

In appendix A.9 we also show that, in certain circumstances, the dynamics generated by the M.E. (4.74) can be non-positive.

4.5. Entropy production

In the previous sections we have observed that, while the Master Equation derived in the weak coupling limit according to the Davies's procedure gives rise to a semigroup of completely positive dynamical maps, the dynamics generated by the M.E. proposed in[31] is *not completely positive* and in some circumstances is *not even positive*. In this section we want to highlight another important consequence of the lack of complete positivity: the violation of the Second Law of Thermodynamics as formulated in 3.3.2, in the context of the Open Quantum Systems; in particular we will see that the non-CP dynamics can be affected by a negative entropy production for a very large and significative set of initial states and for certain values of the bath temperatures and of the applied frequency. In order to accomplish this task, we must find a suitable expression for the entropy production $\sigma(t)$.

4.5.1. Analytical study

The entropy production formula (3.33) is defined through the relative entropy

$$\sigma(\rho) = -\kappa_B \mathrm{Tr}\Big(\mathbf{L}[\rho] \Big(\log\rho - \log\rho_{\mathrm{eq}} \Big) \Big), \quad \mathbf{L}[\rho_{\mathrm{eq}}] = 0\,, \tag{4.82}$$

where ρ_{eq} is the equilibrium state, $\mathbf{L}$ is the total generator. The possible time-dependence is hidden into the $\sigma(t)$ time-dependence, whenever we consider a system evolving in time.

In this section we are only interested in the dependence of σ on the states, since we want to find in which set of states we can have negative entropy production.

Once we express ρ in the Bloch representation with respect to the basis $\sigma^x, \sigma^m, \sigma^n$, the action of the generator $\mathbf{L}$ can be written after the definitions

$$\begin{cases} L_x := L_{10} + L_{11}a + L_{12}b + L_{13}c \\ L_m := L_{20} + L_{21}a + L_{22}b + L_{23}c \\ L_n := L_{30} + L_{31}a + L_{32}b + L_{33}c \end{cases} \quad \Rightarrow \mathbf{L}[\rho] = -2\big(L_x\sigma^x + L_m\sigma^m + L_n\sigma^n\big)\,. \tag{4.83}$$

ρ can be expressed by the following spectral decomposition:

$$\rho = \left(\frac{1+r}{2}\right)\frac{\sigma_0 + \hat{r}\cdot\boldsymbol{\sigma}}{2} + \left(\frac{1-r}{2}\right)\frac{\sigma_0 - \hat{r}\cdot\boldsymbol{\sigma}}{2} \tag{4.84}$$

where $r^2 = a^2 + b^2 + c^2$, $\hat{r} = \frac{\boldsymbol{r}}{r}$ and $\boldsymbol{\sigma} = (\sigma^x, \sigma^m, \sigma^n)$.

Looking at the two eigenvalues in brackets one can notice that:

- they are both positive and ≤ 1 if and only if $0 \leq r \leq 1$;
- each of them is 0 if and only if the other is 1, whenever $r = 1$. In this case the density matrix is a projector and represents a pure state, as expected.

Therefore, for 2-level systems, states are identified by points in the Bloch unit sphere $\{\boldsymbol{r} \in \mathbb{R}^3,\ r^2 \leq 1\}$, with the pure states on the surface.

With this formalism we can calculate the first term in (4.82). First we obtain

$$\begin{aligned} \mathbf{L}[\rho]\cdot\log\rho = -2\big(L_x\sigma^x + L_m\sigma^m + L_n\sigma^n\big)\Bigg[\log\left(\frac{1+r}{2}\right)\left(\frac{\sigma_0}{2} + \frac{a\sigma^x + b\sigma^m + c\sigma^n}{2r}\right) + \\ + \log\left(\frac{1-r}{2}\right)\left(\frac{\sigma_0}{2} - \frac{a\sigma^x + b\sigma^m + c\sigma^n}{2r}\right)\Bigg]\,, \end{aligned} \tag{4.85}$$

and then the trace

$$-\mathrm{Tr}\Big[\mathbf{L}[\rho]\cdot\log\rho\Big] = \frac{2}{r}\log\left(\frac{1+r}{1-r}\right)\Big[aL_x + bL_m + cL_n\Big]\,. \tag{4.86}$$

For the second term in (4.82) we have

$$\mathrm{Tr}\Big[\mathbf{L}[\rho]\cdot\log\rho_{\mathrm{eq}}\Big] = \frac{2}{r_{\mathrm{eq}}}\log\left(\frac{1+r_{\mathrm{eq}}}{1-r_{\mathrm{eq}}}\right)\Big[a_{\mathrm{eq}}L_x + b_{\mathrm{eq}}L_m + c_{\mathrm{eq}}L_n\Big]\,, \tag{4.87}$$

where $r_{\mathrm{eq}} = \sqrt{a_{\mathrm{eq}}^2 + b_{\mathrm{eq}}^2 + c_{\mathrm{eq}}^2}$.

In the end, the final expression is (κ_B-normalized)

$$\begin{aligned} \frac{\sigma(\rho)}{\kappa_B} =& \frac{2}{r}\log\left(\frac{1+r}{1-r}\right)\Big(aL_x + bL_m + cL_n\Big) - \\ & - \frac{2}{r_{\mathrm{eq}}}\log\left(\frac{1+r_{\mathrm{eq}}}{1-r_{\mathrm{eq}}}\right)\Big(a_{\mathrm{eq}}L_x + b_{\mathrm{eq}}L_m + c_{\mathrm{eq}}L_n\Big)\,. \end{aligned} \tag{4.88}$$

First of all we calculate the entropy production for a state chosen as a small perturbation along the $\hat{n}$-axis of the asymptotic state, that we have found in our analysis

$$\rho = \frac{\mathbf{1} - P\sigma^n}{2} + \frac{\epsilon}{2}\sigma^n, \tag{4.89}$$

where the polarization P is given by (4.69):

$$P = \frac{(\omega' - \Omega)^2 J_+ + (\omega' + \Omega)^2 J_-}{(\omega' - \Omega)^2 c_+ J_+ + (\omega' + \Omega)^2 c_- J_-}, \tag{4.90}$$

and is positive and lesser than 1.

The positivity condition for the perturbed density matrix imposes

$$\epsilon \in [-1 + P; 1 + P]\,. \tag{4.91}$$

Inserting (4.89) into (4.88) we have (here and in the following pages $\kappa_B \equiv 1$)

$$\begin{aligned} \sigma(\rho) =& 2L_n\left(\frac{1}{|-P+\epsilon|}\log\left(\frac{1+|-P+\epsilon|}{1-|-P+\epsilon|}\right)(-P+\epsilon) - \log\left(\frac{1+P}{1-P}\right)\right) = \\ =& 2\Big(L_{30} - (P-\epsilon)L_{33}\Big)\log\left(\frac{(1-P+\epsilon)(1+P)}{(1+P-\epsilon)(1-P)}\right). \end{aligned} \tag{4.92}$$

Since $P = L_{30}/L_{33}$ the factor in round brackets is always non-negative if $\epsilon \geq 0$ and the logarithm is non-negative as well, in the same condition. Consequently the Second Law of Thermodynamics cannot be violated.

Remark 4.1. It is very important to notice, however, that if we consider, instead of the asymptotic stationary state ρ_{eq}, the Gibbs thermal state

$$\rho_\beta = \frac{\mathbf{1} - \tanh(\beta\omega'/2)\sigma^n}{2}, \tag{4.93}$$

where β is the inverse temperature of the environment, with respect to the Hamiltonian $H_{\mathrm{eff}} = \omega'/2 \cdot \sigma^n$, then (4.92) becomes negative for

$$\epsilon \in [-\tanh(\beta\omega'/2 + P, 0]\,. \tag{4.94}$$

This is a confirmation that the non-negativity of the entropy production, as a consequence of the Lindblad H-theorem, is verified only when the reference state is stationary. Even though the thermal state converges to the stationary state when $\beta \to \infty$ or $\omega \to 0$, it is immediate to notice that under these conditions the interval of ϵ values that cause the negative entropy production becomes vanishingly small.

Even if the non-completely positive dynamics does not violate the Second Law when considering reference states as small perturbations of the stationary ρ_{eq} along the $\hat{n}$ direction, it turns out that if we perturb ρ_{eq} along the $\hat{m}$ and $\hat{n}$ directions, we do have negative entropy production for a specific set of values of b and c. In fig. 4.1, using Maxima, we have plotted the entropy production as a function of the components b and c and we can observe that there is a region where $\sigma < 0$.

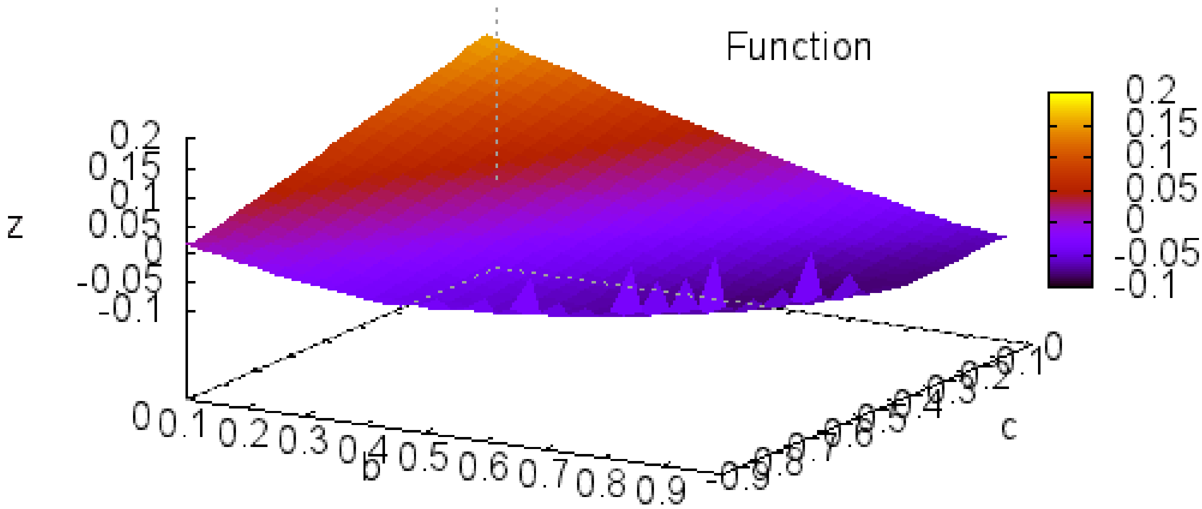


Figure 4.1.: $\sigma(\varrho)$ surface, in units of $\kappa\Delta$. Parameters: $\alpha = 0.005$, $\omega_c = 1000$, $\beta = 100$, $\omega = 2$.

4.5.2. Numerical study

Once the master equation coefficients are known, the full time-evolution $\{\rho(t), t \geq 0\}$ from any chosen initial state ρ_0 can be calculated thanks to an algorithm integrating the equations of motion. In this case, a standard Runge-Kutta algorithm was used, with Klash-Karp fifth order step method and adaptive step size, taken directly from[32]. The entropy production can then be evaluated at each iteration step.

The stationary reference state for the calculation of σ is obtained thanks to the Kramer rule, just after the evaluation of $\{L_{jk}\}$, while the thermal state is calculated thanks to eq. (4.93).

Once $\mathbf{L}$ is calculated for some given values of the parameters β, Ω, Δ, ω_c and α, it is possible to generate a map of σ on all the states in the Bloch sphere, searching for violations of positivity.

The physical quantities entering the model as parameters are:

- Inverse temperature β
- Pumping frequency Ω
- Pumping amplitude Δ; $\omega' = \sqrt{\Omega^2 + \Delta^2}$
- Critical frequency ω_c
- Coupling constant α.

The following adimensional quantities are defined:

$$\begin{aligned} x &:= \Omega/\Delta \quad \Rightarrow \quad \Omega = x\Delta, \quad \omega' = \Delta\sqrt{1+x^2} \\ x_c &:= \omega_c/\Delta \quad \Rightarrow \quad \omega_c = x_c\Delta \\ y &:= \kappa_B T/(\hbar\Delta) \quad \Rightarrow \quad \kappa_B T = y\hbar\Delta \end{aligned} \tag{4.95}$$

The direct inspection of the Master Equation proposed in[31], in its explicit form (A.146), reveals that it can be fully expressed in terms of the above adimensional quantities, plus the coupling constant α which is already adimensional. After the substitutions, an overall factor Δ comes out in front of everything, which is dimensionally consistent with the fact that the Master Equation takes $\rho(t)$ and gives out $\dot{\rho}(t)$. This suggests to parametrize the time t with the adimensional quantity

$$\bar{t} := t\Delta \tag{4.96}$$

Therefore the parameter Δ has the sole physical role of fixing the time scale of the description: once the system is parametrized in terms of the above adimensional quantities Eq. (4.95), varying Δ results only in a dilatation/contraction of the time scale. For this reason, Δ was kept fixed to the value of 1 throughout our investigations, as was done in[31].

Entropy production positivity violations

Our first investigation aimed to create a map of σ over the whole space of states, that is the set of all Bloch vectors with $r < 1$. All pure states are excluded since the practical formula for calculating σ, Eq. (4.88), diverges for $r = 1$.

The implemented program takes the parameters α, ω_c, Ω, Δ and β as input, calculates their adimensional equivalent as to Eq. (4.95), calculates the coefficients $\{L_{jk}\}$ and obtains both the stationary state and the thermal state in the Bloch parametrization. Then it evaluates the entropy production on any chosen state, with respect either to the stationary or to the thermal state.

Here we present only the results obtained with the stationary reference state, believing them to be the most significant as explained previously. In addition, the calculation with the thermal state fails in the high frequency and/or low temperature regime, because $\tanh(\beta\hbar\omega'/2) \to 1$ and ρ_β becomes indistinguishable from a pure state, causing a divergence in Eq. (4.88). The stationary state does not cause such problems because it is never completely pure, for close it may be to the edge of the Bloch sphere.

For every chosen set of the physical parameters, $\sigma[\rho]$ was evaluated in roughly 6 million points randomly selected inside the Bloch sphere. *Some violations of the second law were indeed observed*, with an incidence reaching peaks of 45% of the total number of states, more frequently as the temperature is lowered, while in general no violation was observed for high temperatures.

The most important data are collected in Tables 4.1 and 4.2. Results are displayed only for values of β and Ω that produce a negative entropy production. Furthermore, the tables report also $\langle\sigma\rangle$, the average value of σ, and $\langle \text{neg.}\sigma\rangle$, the average value of σ performed only on states where it is negative, in order to have an idea of the magnitude of the violations. Errors were obtained through statistics; for $\langle\sigma\rangle$ and for $\langle \text{neg.}\sigma\rangle$ they are not displayed, being typically of order of $1\% \sim 0.01\%$.

It is interesting to consider the proximity of ρ_β to ρ_{eq}, measured through the following definition of a *distance* between states, descending from the trace norm:[3]

$$\begin{aligned} d(\rho_1, \rho_2) : &= \|\rho_1 - \rho_2\| = \mathrm{Tr}\sqrt{(\rho_1 - \rho_2)^2} = \\ &= \frac{1}{2}\Big((a_1 - a_2)^2 + (b_1 - b_2)^2 + (c_1 - c_2)^2\Big), \end{aligned} \tag{4.98}$$

the last passage coming from the direct calculation with the Bloch parametrization of ρ_1 and ρ_2. Apart from the factor 1/2, $\|\rho_1 - \rho_2\|$ is nothing but the Euclidean distance between the corresponding points in the Bloch space.

Tables 4.1 and 4.2. We believe the cases when $\|\rho_{\text{eq}} - \rho_\beta\|$ is particularly small to be the most significant, because when $\rho_{\text{eq}} \simeq \rho_\beta$ the physical description is fully adherent to thermodynamics, therefore an observed negative entropy production represents indeed a violation to the Second Law of Thermodynamics as formulated in 3.3.2.

[3] The *trace norm* for a generic operator on some Hilbert space is defined as

$$\|A\| := \mathrm{Tr}\sqrt{A^\dagger A}\,. \tag{4.97}$$

Since density matrices are hermitian and positive-defined, their trace norm is simply the trace.

Ω	$\lVert\rho_\beta - \rho_{\mathrm{eq}}\rVert$	neg. points (%)	$\langle$neg. $\sigma\rangle$	$\langle\sigma\rangle$
		$\beta = 2$		
0.125	0.0097	2.496 ± 0.024	-0.00428	0.07861
0.250	0.0365	2.868 ± 0.011	-0.00419	0.07564
0.500	0.1164	3.733 ± 0.025	-0.00408	0.06822
1.000	0.2581	4.440 ± 0.031	-0.00385	0.05798
2.000	0.3764	3.811 ± 0.024	-0.00321	0.05074
4.000	0.4379	1.874 ± 0.013	-0.00210	0.04676
8.000	0.4688	0.04433 ± 0.00056	-0.00088	0.04441
		$\beta = 5$		
Ω	$\lVert\rho_\beta - \rho_{\mathrm{eq}}\rVert$	neg. points (%)	$\langle$neg. $\sigma\rangle$	$\langle\sigma\rangle$
0.125	0.0019	4.063 ± 0.030	-0.01585	0.10343
0.250	0.0074	6.866 ± 0.016	-0.01842	0.09399
0.500	0.0288	13.15 ± 0.21	-0.02188	0.07570
1.000	0.0981	20.128 ± 0.082	-0.02135	0.05245
2.000	0.2283	23.10 ± 0.19	-0.01724	0.03376
4.000	0.3492	23.855 ± 0.060	-0.01405	0.02405
8.000	0.4226	23.413 ± 0.078	-0.01166	0.01991
		$\beta = 10$		
Ω	$\lVert\rho_\beta - \rho_{\mathrm{eq}}\rVert$	neg. points (%)	$\langle$neg. $\sigma\rangle$	$\langle\sigma\rangle$
0.125	9.13×10^{-5}	3.211 ± 0.026	-0.01988	0.14582
0.250	4.40×10^{-4}	7.725 ± 0.033	-0.02660	0.12478
0.500	0.0015	16.47 ± 0.16	-0.03647	0.10055
1.000	0.0134	26.34 ± 0.17	-0.04116	0.06777
2.000	0.0824	31.55 ± 0.27	-0.03196	0.03542
4.000	0.2241	32.903 ± 0.088	-0.02165	0.01868
8.000	0.3488	33.423 ± 0.19	-0.01635	0.01232

Table 4.1.: Entropy production data for $\simeq 6 \cdot 10^6$ points randomly chosen in the Bloch space. Parameters: $\alpha = 0.005$, $\omega_c = 1000$.

		$\beta = 20$		
Ω	$\|\rho_\beta - \rho_{\rm eq}\|$	neg. points (%)	$\langle$neg. $\sigma\rangle$	$\langle\sigma\rangle$
0.125	2.08×10^{-8}	3.749 ± 0.019	-0.02198	0.14606
0.250	2.03×10^{-7}	8.489 ± 0.024	-0.02887	0.12586
0.500	6.20×10^{-6}	17.25 ± 0.149	-0.03983	0.10505
1.000	4.31×10^{-4}	28.43 ± 0.090	-0.05365	0.07814
2.000	0.0084	36.55 ± 0.45	-0.05636	0.04486
4.000	0.0776	39.16 ± 0.22	-0.03674	0.01978
8.000	0.2231	39.52 ± 0.27	-0.02218	0.00959
		$\beta = 40$		
Ω	$\|\rho_\beta - \rho_{\rm eq}\|$	neg. points (%)	$\langle$neg. $\sigma\rangle$	$\langle\sigma\rangle$
0.125	5.13×10^{-16}	4.038 ± 0.021	-0.02278	0.14479
0.250	3.40×10^{-14}	8.693 ± 0.034	-0.02933	0.12554
0.500	2.66×10^{-11}	17.35 ± 0.13	-0.04011	0.10506
1.000	1.09×10^{-8}	28.537 ± 0.094	-0.05427	0.07849
2.000	1.50×10^{-4}	37.38 ± 0.38	-0.06504	0.04834
4.000	0.0071	42.34 ± 0.21	-0.06135	0.02477
8.000	0.0763	43.69 ± 0.11	-0.03629	0.01018
		$\beta = 80$		
Ω	$\|\rho_\beta - \rho_{\rm eq}\|$	neg. points (%)	$\langle$neg. $\sigma\rangle$	$\langle\sigma\rangle$
0.125	0.	4.115 ± 0.021	-0.02296	0.14451
0.250	0.	8.735 ± 0.036	-0.02942	0.12549
0.500	0.	17.37 ± 0.14	-0.04017	0.10506
1.000	6.94×10^{-15}	28.550 ± 0.095	-0.05434	0.07850
2.000	1.19×10^{-8}	37.40 ± 0.39	-0.06522	0.04839
4.000	1.04×10^{-4}	42.74 ± 0.21	-0.06839	0.02626
8.000	0.0068	45.65 ± 0.15	-0.05992	0.01278

Table 4.2.: Entropy production data for $\simeq 6 \cdot 10^6$ points randomly chosen in the Bloch space. Parameters: $\alpha = 0.005$, $\omega_c = 1000$.

Entropy production time-evolution

Having stated that the model at study may indeed generate a negative entropy production, the question arose whether these violations have only a transient character, vanishing quickly after a short time interval, or can indeed persist in time, even after many pumping cycles. To answer such question we employed the numerical integration algorithm to obtain the time-evolution of $\rho(t)$ from any chosen initial state, and therefore also the time-evolution of $\sigma(t)$.

Results were quite intriguing, especially when compared to the same calculations performed in the completely positive case. To summarize, the completely positive dynamics produces always a $\sigma(t)$ time-evolution curve looking almost like a damped exponential, positive and converging to 0, the expected value for σ in the stationary state. The original master equation has a similar behavior, but in addition the $\sigma(t)$ curve appears often oscillating about an average value that is mostly coincident or very close to the time-evolution curve in the completely positive case. The structure of these oscillations may be very simple and clear, or more irregular and complex, depending on the choice of β, Ω and the initial state, but the main oscillating character is always present and the main frequency is independent of the initial state, the latter often affecting the amplitude instead. In general, the oscillations get clearer and cleaner as the temperature decreases.

Figures 4.2 and 4.3 report two relevant examples, showing in the same graph the $\sigma(t)$ curves for both master equations with the same parameters, in units of $\kappa\Delta$. Figures 4.4 and 4.5 report two examples of $\rho(t)$ time-evolution, expressed through the curves $a(t)$, $b(t)$, $c(t)$ and $r(t)$, the latter serving as a check against positivity violations, occurring for $r > 1$. The simulation time must be intended as the adimensional variable $\bar{t} = t\Delta$. In general there isn't any visible difference between the evolution curves generated by the original master equation and those of the completely positive case; the reported graphs are from the former. Indeed, the direct numerical inspection of the two generators shows they are generally very close: the two central coefficients L_{11} and L_{22} have at best a relative difference around 15% in extremes conditions, while generally being much closer, while all the others entries are always within few per cents of each other. In particular, the coefficients that are 0 in the completely positive master case, are of order 10^{-3} in the other one.

The initial chosen state in the two simulations presented here was the pure state $|z, -\rangle$, following the indications in[31]; in the Bloch parametrization it is expressed by

$$|z, -\rangle \langle z, -| = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} = \frac{\sigma_0 - \sigma^z}{2} = \frac{\sigma_0 - (\Omega\sigma^m + \Delta\sigma^n)/\omega'}{2} \tag{4.99}$$

$$\tag{4.100}$$

therefore the corresponding Bloch vector is

$$-\left(0, \frac{\Omega}{\omega'}, \frac{\Delta}{\Omega'}\right). \tag{4.101}$$

Analyzing Fig. 4.2 one can notice that the oscillations seem to be connected with the observed violations of σ positivity: they bring σ into the negative region, in some cases even after σ has been positive for a considerable number of periods.

Origin of the oscillations

The issue addressed here is the origin of the oscillations observed in $\sigma(t)$ time-evolution generated by the original master equation; more specifically:

- Have they constant frequency? If so, which is the value of the frequency?
- Is it possible to identify a Hamiltonian operator responsible for the oscillations?
- Why do the oscillations not appear in the completely positive case?

The answer turned out to be the following: the oscillations have constant frequency and are due to the Hamiltonian part of the generator $\mathbf{L}$, that is that part of $\mathbf{L}$ whose action on ρ can be written in the form of $-i/2$ times a commutator, equivalent to the action of H_{eff} plus a (usually small) correction coming from the system-environment interaction. This Hamiltonian will be noted with $\tilde{H}$ and $\tilde{\omega}$ will be the associated frequency.[4] The reason why we observe oscillations is that even though $\mathbf{L}[\rho_{\text{eq}}] = 0$, $\tilde{H}$ *does not commute with* ρ_{eq}, in other words ρ_{eq} is not an invariant state for the Hamiltonian part alone of the generator. In the completely positive case this condition is verified instead, as will be discussed in a while.

In order to explain how this result was obtained, a theoretical preamble is needed. Consider the most generic Hamiltonian acting on a spin-1/2 system, in the usual $\{\sigma^x, \sigma^m, \sigma^n\}$ base for the operators:

$$H = \alpha_x \sigma^x + \alpha_m \sigma^m + \alpha_n \sigma^n, \qquad \alpha_x,\, \alpha_m,\, \alpha_n \in \mathbb{R}\,.$$

[4]In this context, the new notation employing ˜ does *not* serve to distinguish quantities in the rotated frame with respect to their counterparts in the original frame; we have been working only in the rotated frame since its introduction.

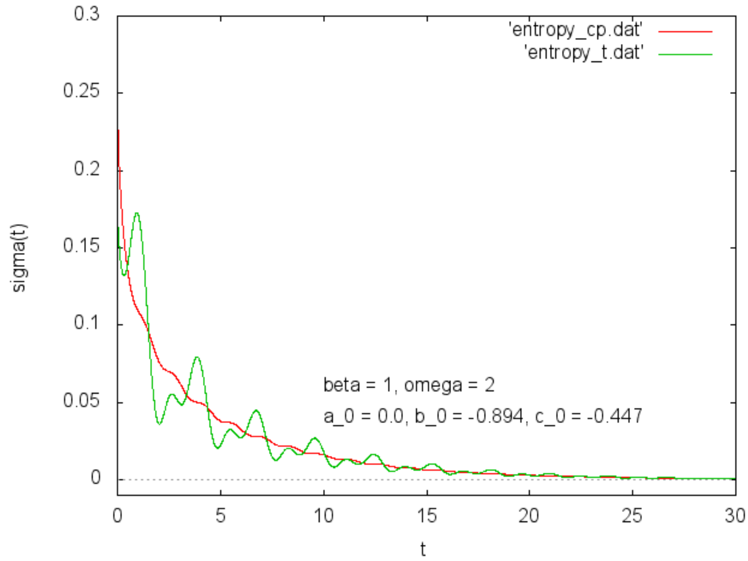


Figure 4.2.: $\sigma(t)$ curves for both master equations, in units of $\kappa\Delta$: the red (darker) curve for the completely positive case, the green (lighter) one from the original master equation. Time-evolution as a function of the adimensional variable $\bar{t} = t\Delta$. Parameters: $\alpha = 0.005$, $\omega_c = 1000$, $\beta = 1$, $\Omega = 2$; initial state: $|z, -\rangle$, whose Bloch vector is written in the figure.

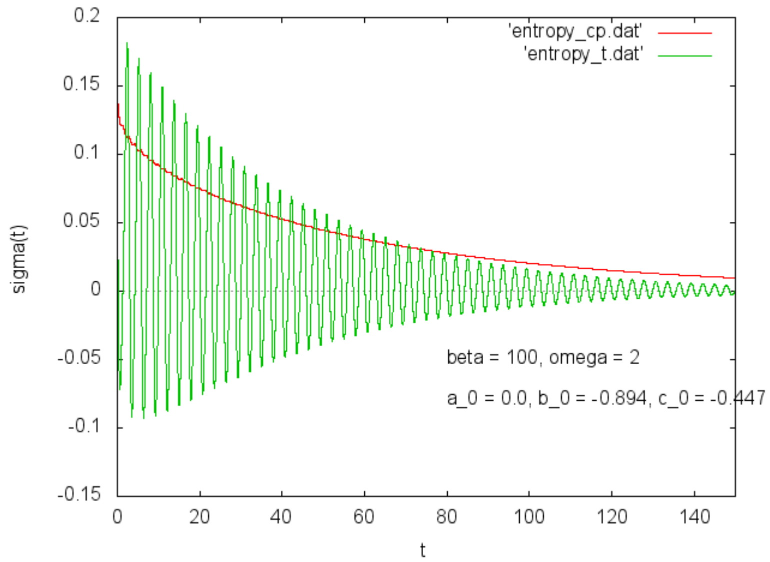


Figure 4.3.: $\sigma(t)$ curves for both master equations in units of $\kappa\Delta$. Parameters: $\alpha = 0.005$, $\omega_c = 1000$, $\beta = 100$, $\Omega = 2$; initial state: $|z, -\rangle$, the corresponding Bloch vector is written in the figure.

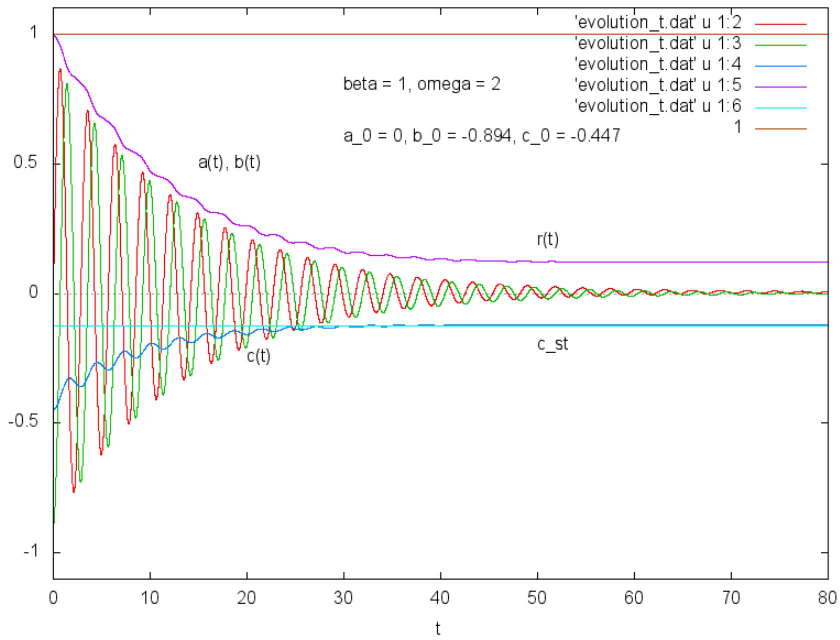


Figure 4.4.: Example of $\rho(t)$ time-evolution. Parameters: $\alpha = 0.005$, $\omega_c = 1000$, $\beta = 1$, $\Omega = 2$; initial state: $|z, -\rangle$.

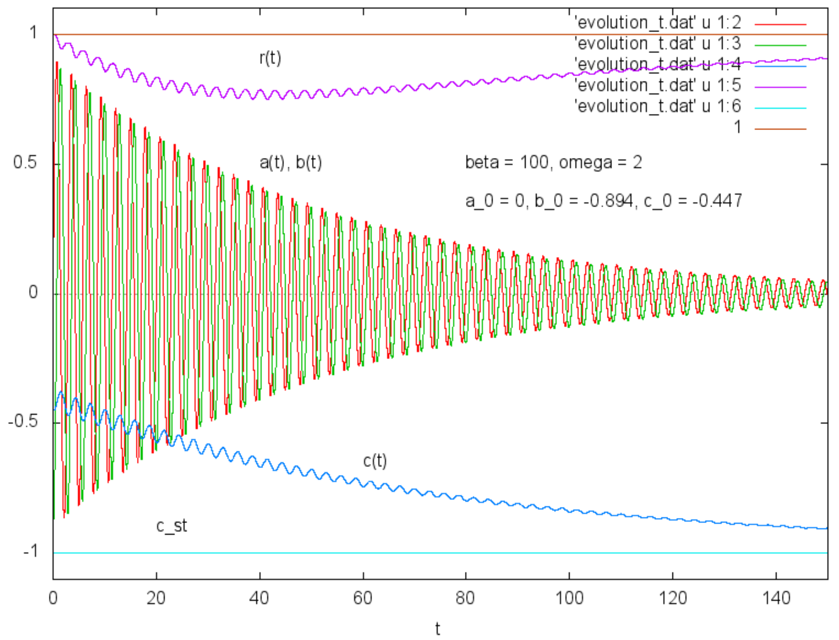


Figure 4.5.: Example of $\rho(t)$ time-evolution. Parameters: $\alpha = 0.005$, $\omega_c = 1000$, $\beta = 100$, $\Omega = 2$; initial state: $|z, -\rangle$.

Its action on whatever state through the commutator $-i/2[H,\cdot]$ can be expressed as a 4×4 matrix acting from the left on a Bloch state:

$$-\frac{i}{2}[H,\cdot] \quad \Leftrightarrow \quad \frac{1}{2}\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & -\alpha_n & \alpha_m \\ 0 & \alpha_n & 0 & -\alpha_x \\ 0 & -\alpha_m & \alpha_x & 0 \end{pmatrix}. \tag{4.102}$$

This is the most general form of antisymmetric matrix acting on a Bloch vector, therefore we conclude that every Hamiltonian can always be expressed as a fully antisymmetric matrix. The vice versa is also true: any antisymmetric matrix can be uniquely associated to a certain Hamiltonian, acting on density matrices via $-i/2$ times the commutator.

The generic antisymmetric matrix Eq. (4.102), corresponding to H, can always be diagonalized:

$$\begin{aligned} & H\left|v_{1,2}\right\rangle = \epsilon_{1,2}\left|v_{1,2}\right\rangle \\ \Rightarrow \quad & H = \epsilon_1 P_1 + \epsilon_2 P_2, \qquad P_{1,2} = \left|v_{1,2}\right\rangle\left\langle v_{1,2}\right| \end{aligned}$$

and since $\mathrm{Tr}H = 0$ and $\mathrm{Tr}P_{1,2} = 1$, it follows $\epsilon_1 = -\epsilon_2$, so one can choose $\epsilon_1 \equiv \epsilon > 0$ and $\epsilon_2 \equiv -\epsilon$, whence

$$H = \epsilon(P_1 - P_2)\,. \tag{4.103}$$

The direct calculation leads finally to

$$\epsilon = \frac{1}{2}\sqrt{\alpha_x^2 + \alpha_m^2 + \alpha_n^2} \quad \Rightarrow \quad P_{1,2} = \frac{\sigma_0 \pm H/\epsilon}{2}\,. \tag{4.104}$$

Let us focus now on the Hamiltonian part of the generator $\mathbf{L}$, that is $\tilde{H}$, which can be calculated by taking the antisymmetric part of $\mathcal{L}$, the matrix representing $\mathbf{L}$:

$$\mathcal{L}_A = -\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & L_{12} - L_{21} & L_{13} - L_{31} \\ 0 & L_{21} - L_{12} & 0 & L_{23} - L_{32} \\ 0 & L_{31} - L_{13} & L_{32} - L_{23} & 0 \end{pmatrix}$$

and comparing this to Eq. (4.102) leads to

$$\begin{cases} \alpha_x = 2(L_{23} - L_{32}) \\ \alpha_m = -2(L_{13} - L_{31}) \\ \alpha_n = 2(L_{12} - L_{21})\,. \end{cases} \tag{4.105}$$

Finally, by identifying the energy ϵ with $\tilde{\omega}$, one finds the real intrinsic frequency of the Hamiltonian affecting the system.

It is also possible to calculate the thermal state given by $\tilde{H}$, employing Eq. (4.104):

$$\begin{aligned} \tilde{\rho}_\beta &= \frac{e^{-\beta\tilde{H}}}{\mathrm{Tr}e^{-\beta\tilde{H}}} = \frac{e^{-\beta\epsilon/2}P_1 + e^{\beta\epsilon/2}P_2}{2\cosh{(\beta\epsilon/2)}} = \\ &= \frac{\sigma_0 - \tanh{(\beta\epsilon/2)}\tilde{H}/\epsilon}{2} \end{aligned} \tag{4.106}$$

$$\Rightarrow \quad \tilde{a}_\beta = -\frac{\alpha_x}{\epsilon}\tanh\left(\frac{\beta\epsilon}{2}\right), \qquad \tilde{b}_\beta = -\frac{\alpha_m}{\epsilon}\tanh\left(\frac{\beta\epsilon}{2}\right), \qquad \tilde{c}_\beta = -\frac{\alpha_n}{\epsilon}\tanh\left(\frac{\beta\epsilon}{2}\right)$$

One can now compare this new thermal state to ρ_β, the one obtained from H_{eff}, as well as the frequencies $\tilde{\omega}$ and ω'. Results for the first comparison do not offer any surprise: since the coupling is weak, $\tilde{H}$ is actually very close to H_{eff}, and so $\tilde{\rho}_\beta$ is very close to ρ_β.

The frequencies deserve closer attention because of their relation with the observed frequencies ω_m of $\sigma(t)$ oscillations, which were obtained by measuring the time interval between two subsequent maximum points while running the simulations. The agreement between ω', $\tilde{\omega}$ and the measured frequency is indeed very good: the relative differences

$$\delta' = \frac{|\omega' - \omega_m|}{\omega'}, \qquad \tilde{\delta} = \frac{|\tilde{\omega} - \omega_m|}{\tilde{\omega}} \tag{4.107}$$

never exceed 7% and in most cases are below 1%, as shown in Table 4.3, presenting three examples at very high, intermediate and very low temperature.

As can can be seen from the figures, ω_m is usually closer to $\tilde{\omega}$ than to ω', but not always. The three frequencies are always very close to each other.

In all these computations the initial state was $(0.2, 0.2, -0.7)$, because it seemed to produce the largest and cleanest oscillations. Other states produced often more complex secondary structures between the main oscillation peaks, therefore even though the main oscillating pattern is still recognizable, in practice it is more difficult to measure the frequency. Since the oscillations are clearer and cleaner for low temperatures and for high frequencies, in the case $\beta = 1$ it was not possible to measure ω_m for $\omega < 1$.

The last issue to be faced is the fact that $[\tilde{H}, \rho_{\mathrm{eq}}] \neq 0$: this was verified numerically, comparing also the original master equation to the completely positive case, for which instead the commutator is 0. In the latter case in fact the stationary state is *exactly* polarized along σ^n and since the coefficients L_{13}, L_{23}, L_{31} and L_{32} are identically 0, the antisymmetric part of the generator can only have the coefficient α_n different from 0, so the corrected Hamiltonian is also polarized along σ^n, see Eq. (4.102) and (4.105).

Ω	ω'	$\tilde{\omega}$	ω_m	δ'	$\tilde{\delta}$
			$\beta = 1$		
Ω	ω'	$\tilde{\omega}$	ω_m	δ'	$\tilde{\delta}$
1.000	1.41421	1.37902	1.3706±0.0025	0.0318	0.00612
2.000	2.23607	2.21395	2.1978±0.0046	0.0175	0.00739
4.000	4.12310	4.11111	4.0934±0.0060	0.00726	0.00433
8.000	8.06226	8.05609	8.0443±0.0059	0.00223	0.00146
			$\beta = 10$		
Ω	ω'	$\tilde{\omega}$	ω_m	δ'	$\tilde{\delta}$
0.125	1.00778	0.94521	0.94527±0.00039	0.0661	0.000057
0.250	1.03078	0.96933	0.96945±0.00065	0.0633	0.000122
0.500	1.11803	1.06051	1.06112±0.00084	0.0536	0.000576
1.000	1.41421	1.36703	1.3678±0.0010	0.0339	0.000565
2.000	2.23607	2.20488	2.2059±0.0011	0.0137	0.000436
4.000	4.12311	4.10574	4.105352±0.000049	0.00433	0.000095
8.000	8.06226	8.05327	8.0514±0.0040	0.00135	0.000236
			$\beta = 100$		
Ω	ω'	$\tilde{\omega}$	ω_m	δ'	$\tilde{\delta}$
0.125	1.00778	0.94486	0.94372±0.00024	0.0679	0.00121
0.250	1.03078	0.96892	0.96869±0.00094	0.0641	0.000242
0.500	1.11803	1.05986	1.06049±0.00070	0.0542	0.000601
1.000	1.41421	1.36567	1.36613±0.00072	0.0352	0.000334
2.000	2.23607	2.20256	2.2027±0.0014	0.0151	0.000080
4.000	4.12311	4.10317	4.1027±0.0017	0.00497	0.000112
8.000	8.06226	8.05123	8.05169±0.00019	0.00131	0.000057

Table 4.3.: Comparison between the system Hamiltonian frequency, the full generator frequency and the observed frequency in $\sigma(t)$ oscillations. Parameters: $\omega_c = 1000$, $\alpha = 0.005$; initial state: (0.2,0.2,-0.7).

The commutator $-i[\tilde{H}, \rho_{\mathrm{eq}}]$ was computed by calculating the matrix Eq. (4.102) and making it acting on ρ_{eq} from the left. The x and m values of the resulting vector represent the magnitude of the "commutativity violation", which showed to be generally of the same order of magnitude as the coefficients L_{13}, L_{23}, L_{31} and L_{32}, that is roughly $10^{-4} \sim 10^{-2}$, which is not surprising since P is typically of order 1. By comparison, the action of $\mathbf{L}[\rho_{\mathrm{eq}}]$ is always not much bigger than the machine precision, roughly $10^{-18} \sim 10^{-19}$.

Remark 4.2. As Fig. 4.2 and 4.3 show, the completely positive dynamics may produce slight oscillations as well. This fact can be understood inspecting the generator $\mathbf{L}_{CP}$,

$$\dot{\rho} = -2\mathbf{L}_{CP}[\rho] \tag{4.108}$$

which, representing $\mathbf{L}_{CP}$ with the matrix $\mathcal{L}_{CP}$, reads:

$$\begin{pmatrix} 1 \\ \dot{a}(t) \\ \dot{b}(t) \\ \dot{c}(t) \end{pmatrix} = -4\mathcal{L}_{CP} \begin{pmatrix} 1 \\ a(t) \\ b(t) \\ c(t) \end{pmatrix} = -4 \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & L_{11} & L_{12} & 0 \\ 0 & L_{21} & L_{22} & 0 \\ L_{30} & 0 & 0 & L_{33} \end{pmatrix} \begin{pmatrix} 1 \\ a(t) \\ b(t) \\ c(t) \end{pmatrix} . \tag{4.109}$$

$\mathcal{L}_{CP}$ can be rewritten in the following form, where the symmetric and antisymmetric part are made explicit:

$$-4\mathcal{L}_{CP} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & L_{11} & s+\tilde{\omega} & 0 \\ 0 & s-\tilde{\omega} & L_{22} & 0 \\ L_{30} & 0 & 0 & L_{33} \end{pmatrix} , \tag{4.110}$$

where $s = (L_{12} + L_{21})/2$ and $\tilde{\omega} = (L_{12} - L_{21})/2$.

Let us introduce the matrix

$$\mathcal{D}_3 = \begin{pmatrix} L_{11} & s+\tilde{\omega} & 0 \\ s-\tilde{\omega} & L_{22} & 0 \\ 0 & 0 & L_{33} \end{pmatrix} , \tag{4.111}$$

thanks to which Eq. (4.109) reads

$$\begin{pmatrix} \dot{a}(t) \\ \dot{b}(t) \\ \dot{c}(t) \end{pmatrix} = -4\mathcal{D}_3 \begin{pmatrix} a(t) \\ b(t) \\ c(t) \end{pmatrix} - 4L_{33} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} , \tag{4.112}$$

To solve this inhomogeneous system of linear differential equations, one needs to find the general solution of the associated homogeneous system and add a particular solution of the inhomogeneous. The latter is readily provided by the known stationary solution:

$$\begin{pmatrix} a_{\rm eq} \\ b_{\rm eq} \\ c_{\rm eq} \end{pmatrix} = -\frac{L_{30}}{L_{33}} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} , \tag{4.113}$$

since $P = L_{30}/L_{33}$; the general solution then formally reads

$$\begin{pmatrix} a(t) \\ b(t) \\ c(t) \end{pmatrix} = e^{-4\mathcal{D}_3 t} \begin{pmatrix} \bar{a} \\ \bar{b} \\ \bar{c} \end{pmatrix} - \frac{L_{30}}{L_{33}} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \tag{4.114}$$

with $(\bar{a}, \bar{b}, \bar{c})$ some vector to be determined from the initial conditions; denoting them by (a_0, b_0, c_0) and substituting them into the above expression, one finds

$$\begin{pmatrix} a(t) \\ b(t) \\ c(t) \end{pmatrix} = e^{-4\mathcal{D}_3 t} \begin{pmatrix} a_0 \\ b_0 \\ c_0 \end{pmatrix} - \frac{L_{30}}{L_{33}} \left(1 - e^{-4L_{33}t}\right) \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} . \tag{4.115}$$

Now the spectrum of $\mathcal{D}_3$ has to be examined: it turns out to be

$$\lambda_\pm = \frac{L_{11} + L_{22} \pm \sqrt{(L_{11} - L_{22})^2 + 4(s^2 - \Omega^2)}}{2} , \qquad \lambda_3 = L_{33} \tag{4.116}$$

and one concludes that $\mathbf{L}_{CP}$ may produce oscillations only if the initial vector has a zero (or small) c_0 component: only $a(t)$ and $b(t)$ can oscillate because $\lambda_\pm$ can be complex, whereas λ_3 is always real. In addition, the time-evolution will eventually drive every initial state towards the equilibrium one, which is polarized along σ_n, therefore, as the system approaches equilibrium and $a(t), b(t) \to 0$, one may expect the oscillations to disappear.

4.6. Conclusions

In this chapter, which presents the main result of this thesis, we have studied a model of minimal circuit immersed in a dissipative thermal bath and driven by an applied alternating potential. This concrete case of open quantum system has already been the subject of an article published in 2011 [31]. The authors of the model proposed a Master Equation to describe the time-evolution of the system from which an approximated expression of the asymptotic steady current is derived.

The Master Equation turns out to generate a non-completely positive reduced dynamics. In view of the considerations exposed in Chap. 3, it was interesting to investigate whether the lack of the complete positivity requirement may lead, in the case at hands, to the violation of the Second Law of Thermodynamics, more concretely if it causes a negative entropy production. Our study showed that, indeed, the dynamics determined by the Master Equation proposed in the original article does violate the Second Law, to an extent depending on how the physical paramaters (temperature, pumping frequency and amplitude) are varied. In particular these violations appear to be very strong when the temperature is very low while they vanish for high ones.

By means of both analytical and numerical investigation of the time-evolution of the system state and of its entropy production, we have compared the behaviour of the original M.E. with another Master Equation that we have derived in the weak coupling limit, following the prescription of eliminating the fast oscillating terms in the generator of the dynamics by taking an ergodic average. By construction, the resulting dynamics is completely positive, hence positive, while the original one also suffers of the lack of positivity in certain circumstances (which means that it maps some physical states onto non positive density matrices, that cannot be admissable physical states). As expected from the application of the Lindblad-H theorem, the complete positive dynamics is not affected by negative entropy production, even though the asymptotic stationary state turns out to be the same, and consequently the steady current.

The results of this work will appear in an article in preparation, with the precious contributions of Marco Pezzutto and my supervisor, Fabio Benatti.

Chapter 5.

Entangled identical particles and noise

While for many decades entanglement has been just an epistemological curiosity, in recent times it is becoming an experimentally accessible resource; in particular, entangled N-qubit states have been proposed as means to beat the so-called shot-noise limit accuracy in parameter estimation. The literature on quantum parameter estimation and metrological applications of many body systems is vast: see for example [33–56] and references therein. Notable steps in this direction using many-body systems have been recently realized: entangled states in systems of ultra-cold atoms have been generated through spin-squeezing techniques [55],[56]. The aim is to use them as input states in interferometric apparatuses, specifically constructed for quantum enhanced metrological applications. In such devices, the initial N-qubit states are rotated by means of collective pseudo-spin operators; for distinguishable qubits, the relevance of entangled states is readily exposed by addressing single particle contributions to the collective operators [46, 54]; however, in the case of trapped ultra-cold atoms, the qubits involved are identical and thus not addressable, a fact that has often not been fully appreciated in the recent literature on quantum metrology and that has been tackled in Refs. [57, 58].

In this chapter, we characterize the entangled states of N boson systems according to the generalized notion of separability given in Ref. [57]; in particular, we show that the negativity, which measures the lack of positivity of partially transposed states, is an exhaustive bipartite entanglement witness. This is to be contrasted with the case of distinguishable qubits where, apart for two qubits or one qubit and one qutrit, there exist entangled states with zero negativity [59].

Then, we show that a purely dephasing noise which, for distinguishable qubits, is responsible for mere decoherence, in the framework of identical bosons can instead generate entanglement; however, we also show that this noise-induced entanglement cannot be used to improve on the sensitivities of matter interferometric devices based on such systems [60].

5.1. Entanglement of identical bosons

The definition of entanglement for the states of a system composed of N *distinguishable* particles is based on the tensor product structure of the total Hilbert space of the system: $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2 \otimes \ldots \otimes \mathcal{H}_N$, where $\mathcal{H}_i$ is the Hilbert space of the i-th particle states. Then, if ρ is the density matrix representing a generic state of the N-particle system, the state is said *separable* if it can be written as a convex linear combination of the single-particle states,

$$\rho = \sum_{i=1,\ldots,N} p_i \rho_i^{(1)} \otimes \rho_i^{(2)} \otimes \ldots \otimes \rho_i^{(N)}, \quad p_i \geq 0, \quad \sum_{i=1,\ldots,N} p_i = 1, \tag{5.1}$$

otherwise the state ρ is said to be *entangled.*

The tensor product structure of $\mathcal{H}$ allows to define linear local operations on the system, i.e. maps of the form

$$\Lambda = \Lambda^{(1)} \otimes \Lambda^{(2)} \otimes \ldots \otimes \Lambda^{(N)} \ , \tag{5.2}$$

where the linear map $\Lambda^{(i)} : \rho^{(i)} \mapsto \Lambda^{(i)}\left[\rho^{(i)}\right]$ acts only upon the i-th particle density matrix.

It is also known, however, that the Hilbert space of a system of *identical* bosons is not given by the tensor product of the single-particle Hilbert spaces, but is formed by the subspace of it spanned by the symmetric combinations of tensor products of the single-particle vectors. For example, the Hilbert space for two identical bosonic qubits is the subspace of $\mathbb{C}^4$ spanned by

$$|\uparrow\uparrow\rangle, \quad |\downarrow\downarrow\rangle, \quad \frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}}, \tag{5.3}$$

where $|i\rangle$, $i = \uparrow, \downarrow$, is any orthonormal basis in $\mathbb{C}^2$. Coherently, a mixed state for identical bosons must be a linear convex combination of projections $|\psi\rangle\langle\psi|$ onto symmetrized vectors.

Consequently, eq. (5.1) cannot be a valid definition of separable state for a system of N identical particles, which is also evident from the fact that, even after a symmetrization, it would remain a mixture of states where the single particles can be distinguished by the labels. Furthermore, also states of the form

$$\rho = \sum_i p_i \, \rho_i \otimes \rho_i \otimes \ldots \otimes \rho_i \ , \tag{5.4}$$

cannot be, in general, admissable states for a system of identical particles. This fact can be clarified using again the example of two identical bosonic qubits. Indeed, any element

$\rho_i^{(1)} \otimes \rho_i^{(2)}$ of the convex sum

$$\rho = \sum_i p_i \rho_i^{(1)} \otimes \rho_i^{(2)}, \tag{5.5}$$

is a 4×4 generic density matrix, as their linear convex combination ρ. Therefore it cannot be written, in general, as a convex combination of solely projections onto the symmetric states.

The notion of entanglement in many-body systems has been addressed and discussed in literature (see, for instance, Ref.[61–76]), however, only limited results actually apply to the case of identical particles. In Ref. [57] a notion of separability based on *algebraic bipartition* has been proposed, that will be briefly illustrated in the following.

Given a system of particles and its Hilbert space $\mathcal{H}$, let us denote with $\mathcal{B}(\mathcal{H})$ the algebra of all bounded operators on it. We give the following definitions.

- An *algebraic bipartition* of the algebra $\mathcal{B}(\mathcal{H})$ is any pair $(\mathcal{A}, \mathcal{B})$ of *commuting subalgebras* of $\mathcal{B}(\mathcal{H})$.[1]
- An element (operator) of $\mathcal{B}(\mathcal{H})$ is said to be *local* with respect to the bipartition $(\mathcal{A}, \mathcal{B})$ if it is the product AB of an element A of $\mathcal{A}$ and another B of $\mathcal{B}$.
- A state ω on the algebra $\mathcal{B}(\mathcal{H})$ will be called *separable* with respect to the bipartition $(\mathcal{A}, \mathcal{B})$ if the expectation $\omega(AB)$ of any local operator AB can be decomposed into a linear convex combination of products of expectations:

$$\omega(AB) = \sum_k \lambda_k \, \omega_k^{(1)}(A) \, \omega_k^{(2)}(B) \ , \qquad \lambda_k \geq 0 \ , \quad \sum_k \lambda_k = 1 \tag{5.6}$$

  where $\omega_k^{(1)}$ and $\omega_k^{(2)}$ are states on $\mathcal{B}(\mathcal{H})$; otherwise the state ω is said to be *entangled* with respect the bipartition $(\mathcal{A}, \mathcal{B})$.

The new definition of entanglement reduces to the standard notion of entanglement for distinguishable particles. For instance, in the case of a two qubit system, by choosing the algebraic bipartition $\mathcal{A} = \mathcal{B} = M_2(\mathbb{C})$, where $M_2(\mathbb{C})$ is the algebra of 2×2 matrices over $\mathbb{C}^2$, and the expectation value $\omega(AB) = \mathrm{Tr}\,(\rho\, A \otimes B)$ defined in the usual way through the trace with the two-qubit density matrix ρ, condition (5.6) readily gives that ρ must be a convex combination of product states.

One can apply the previous notions of separability and entanglement to the case of a system of N bosons confined in an optical trap, for instance a system of N cold atoms trapped in a double-well potential. The dynamics of this kind of system can be very well described by a *Bose-Hubbard* Hamiltonian, that in second quantization assumes the

[1] Notice that the two subalgebras $\mathcal{A}$ and $\mathcal{B}$ need not reproduce the whole algebra $\mathcal{B}(\mathcal{H})$, i.e. in general $\mathcal{A} \cup \mathcal{B} \subset \mathcal{B}(\mathcal{H})$. In this respect, the term "bipartition" is not strictly appropriate and has been adopted for sake of simplicity. However, in the case of the system discussed below, the considered mode partitions actually generate the whole algebra $\mathcal{B}(\mathcal{H})$.

form:

$$H_{\mathrm{BH}} = \epsilon_a a^\dagger a + \epsilon_b b^\dagger b + U((a^\dagger a)^2 + (b^\dagger b)^2) - J(a^\dagger b + a b^\dagger), \tag{5.7}$$

where the first two terms are the contributions of the trapping potential and are proportional to the depths of the wells ϵ_a, ϵ_b; the last term is a hopping term proportional to the *tunneling amplitude* J and the remaining term, which is quadratic in the number operators, describes the repulsive Coulomb interactions inside each well. Usually symmetric double-well potential are considered, where $\epsilon_a = \epsilon_b = \epsilon$.

In this situation, the states $|i\rangle$, $i =\uparrow, \downarrow$, describing one atom located within the left, respectively the right well, correspond to two spatial modes and are created by the action on the vacuum state $|0\rangle$ of creation operators $a^\dagger$, $b^\dagger$: $a^\dagger|0\rangle = |\downarrow\rangle$, $b^\dagger|0\rangle = |\uparrow\rangle$.

When the total number N is conserved, the symmetric Fock space of this two-mode system is generated by the $N+1$ orthonormal vectors:

$$|k, N-k\rangle_{\mathcal{AB}} = \frac{(a^\dagger)^k (b^\dagger)^{N-k}}{\sqrt{k!(N-k)!}}\,|0\rangle \ , \quad 0 \le k \le N \ . \tag{5.8}$$

When the tunneling term can be neglected, these states are eigenstates of the Bose-Hubbard Hamiltonian.

Because of the orthogonality of the spatial modes, by considering the norm-closures of all polynomials P_a in $a, a^\dagger$, respectively P_b in $b, b^\dagger$, one obtains two commuting subalgebras $\mathcal{A}$ and $\mathcal{B}$ that in turn generate the whole algebra of bounded operators for this two mode bosonic system.

One can show that $(\mathcal{A}, \mathcal{B})$-separable density matrices must be convex combinations of projections $|k, N-k\rangle_{\mathcal{AB}}\langle k, N-k|$ (see Ref. [57]):

$$\rho = \sum_{k=0}^{N} p_k |k, N-k\rangle_{\mathcal{AB}}\langle k, N-k| \ , \qquad p_k > 0 \ , \quad \sum_{k=0}^{N} p_k = 1 \ . \tag{5.9}$$

This is so because $\mathcal{A}$ and $\mathcal{B}$ generate the whole two-mode N-boson algebra so that the only pure $(\mathcal{A}, \mathcal{B})$-separable states are projections onto the eigenstates (5.8) of the number operator $a^\dagger a + b^\dagger b$ which thus span the convex subset of $(\mathcal{A}, \mathcal{B})$-separable mixed states.

5.1.1. Negativity

For bipartite systems of distinguishable particles one knows that states ρ that do not remain positive under partial transposition are entangled [59] and are witnessed by the so-called *negativity*:

$$\mathcal{N}(\rho) = \|\rho^\Gamma\|_1 - 1 \ , \qquad \|\rho^\Gamma\|_1 = \mathrm{Tr}\Big(\sqrt{(\rho^\Gamma)^\dagger \rho^\Gamma}\Big) \tag{5.10}$$

where ρ^Γ is the transposition with respect to the first party.

Since $\mathrm{Tr}(\rho) = \mathrm{Tr}(\rho^\Gamma) = 1$, if ρ does not remain positive under partial transposition, then $\|\rho^\Gamma\|_1 > 1$ and $\mathcal{N}(\rho) > 0$. Indeed, let $\rho^\Gamma = \sum_k \lambda_k \, |\psi_k\rangle \, \langle\psi_k|$ be the spectral decomposition of ρ^Γ ($\{|\psi_k\rangle\}_k$ o.n.b. of eigenvectors of ρ^Γ), then

$$\sqrt{(\rho^\Gamma)^\dagger \, \rho^\Gamma} = \sum_k |\lambda_k| \, |\psi_k\rangle \, \langle\psi_k| \,, \tag{5.11}$$

hence

$$\mathcal{N}(\rho) = \sum_k |\lambda_k| - 1 = \sum_k (|\lambda_k| - \lambda_k) > 0 \quad \Leftrightarrow \quad \exists\, \lambda_{\bar{k}} < 0 \quad \text{for some}\, \bar{k}. \tag{5.12}$$

Unfortunately, there can be entangled states that remain positive under partial transposition whence $\mathcal{N}(\rho) = 0$; therefore, the negativity is not an exhaustive entanglement witness for generic bipartite states of distinguishable particles.

Remarkably, negativity is instead an exhaustive entanglement witness for the case at hands: indeed, by performing the partial transposition with respect to the first mode of a generic two mode N-Boson state

$$\rho = \sum_{k,\ell=0}^{N} \rho_{k\ell} |k, N-k\rangle_{\mathcal{AB}} \langle \ell, N-\ell| \ , \qquad \sum_{k=0}^{N} \rho_{kk} = 1 \ , \tag{5.13}$$

one obtains an operator on a larger Hilbert space than the sector of the Fock space with fixed N, namely

$$\rho^\Gamma = \sum_{k,\ell=0}^{N} \rho_{k\ell} |\ell, N-k\rangle_{\mathcal{AB}} \langle k, N-\ell| \ , \tag{5.14}$$

which is such that

$$(\rho^\Gamma)^\dagger \rho^\Gamma = \sum_{k,\ell} |\rho_{k\ell}|^2 \, |k, N-\ell\rangle_{\mathcal{AB}} \langle k, N-\ell| \ , \tag{5.15}$$

whence the negativity

$$\mathcal{N}(\rho) = \sum_{k\neq\ell=0}^{N} \Big|\rho_{k\ell}\Big| \tag{5.16}$$

vanishes if and only if ρ has null off-diagonal element with respect to the Fock states relative to the chosen bipartition, i.e. it is separable because of the form (5.9).

It is important to stress that negativity is always related to a given algebraic bipartition: a state which is entangled with respect to the bipartition $(\mathcal{AB})$ can be separable with respect to another bipartition $(\mathcal{C},\mathcal{D})$.

While the Fock number states (5.8) are $(\mathcal{A},\mathcal{B})$-separable, important examples of $(\mathcal{A},\mathcal{B})$-entangled states are the so-called discrete coherent states

$$|\xi,\varphi\rangle_{\mathcal{AB}} = \frac{1}{\sqrt{N!}}\left(\sqrt{\xi}e^{-i\varphi/2}\,a^\dagger + \sqrt{1-\xi}e^{i\varphi/2}\,b^\dagger\right)^N|0\rangle \tag{5.17}$$

$$= \sum_{k=0}^{N}\sqrt{\binom{N}{k}}\xi^{k/2}(1-\xi)^{(N-k)/2}\,e^{-ik\varphi+iN\varphi/2}\,|k,N-k\rangle_{\mathcal{AB}}, \tag{5.18}$$

where $0\leq\xi\leq 1$. These states describe the situation when all N boson are in the same single particle state $(\sqrt{\xi}\exp(-i\varphi/2)\,,\,\sqrt{1-\xi}\exp(i\varphi/2))$: their off-diagonal elements do not vanish. Therefore, the corresponding negativity is also non-vanishing; indeed, it reads

$$\mathcal{N}\Big(|\xi,\varphi\rangle_{\mathcal{AB}}\langle\xi,\varphi|\Big) = \sum_{k\neq\ell}\sqrt{\binom{N}{k}\binom{N}{\ell}}\xi^{(k+\ell)/2}(1-\xi)^{N-(k+\ell)/2}\,. \tag{5.19}$$

The Bogolubov transformation

$$c=\frac{a+b}{\sqrt{2}}\,,\quad d=\frac{a-b}{\sqrt{2}}\,, \tag{5.20}$$

changes the spatial modes a,b into energy modes; indeed, it corresponds to a change of basis from that of spatially localized states, to the one of the eigenstates

$$c^\dagger\,|0\rangle=\frac{|\downarrow\rangle+|\uparrow\rangle}{\sqrt{2}},\quad d^\dagger\,|0\rangle=\frac{|\downarrow\rangle-|\uparrow\rangle}{\sqrt{2}}, \tag{5.21}$$

of the Bose-Hubbard Hamiltonian when the tunneling term can be neglected:

$$H_{BH}\left(c^\dagger\,|0\rangle\right)=1/\sqrt{2}(\epsilon+U)\left(c^\dagger\,|0\rangle\right),\quad H_{BH}\left(c\,|0\rangle\right)=1/\sqrt{2}(\epsilon-U)\left(c\,|0\rangle\right). \tag{5.22}$$

The algebras $\mathcal{C}$, respectively $\mathcal{D}$, constructed by means of polynomials in $c,c^\dagger$, respectively $d,d^\dagger$, commute, generate the two-mode N Boson algebra and thus provide another possible algebraic bipartition. It thus turn out that the $(\mathcal{A},\mathcal{B})$-entangled coherent state

$$|1/2,0\rangle_{\mathcal{AB}}=\frac{1}{\sqrt{N!}}\Big(\frac{a^\dagger\,+\,b^\dagger}{\sqrt{2}}\Big)^N=\frac{(c^\dagger)^N}{\sqrt{N!}}|0\rangle, \tag{5.23}$$

results the Fock number state $|N,0\rangle_{\mathcal{CD}}$ for the number operator $c^\dagger\,c+d^\dagger\,d$, and therefore it results $(\mathcal{C},\mathcal{D})$-separable. Thus, when we refer to the negativity of a state ρ, one must specify with respect to which algebraic bipartition the partial transposition is performed;

indeed,

$$\mathcal{N}_{\mathcal{AB}}\Big(|1/2,0\rangle_{\mathcal{AB}}\langle 1/2,0|\Big) > 0 \quad \text{while} \quad \mathcal{N}_{\mathcal{CD}}\Big(|1/2,0\rangle_{\mathcal{AB}}\langle 1/2,0|\Big) = 0. \tag{5.24}$$

As another instance of the dependence of the notions of entanglement and non-locality on the chosen bipartition, consider the operators

$$J_x = \frac{1}{2}(a^\dagger b + a b^\dagger)\ ,\ J_y = \frac{1}{2i}(a^\dagger b - a b^\dagger)\ ,\ J_z = \frac{1}{2}(a^\dagger a - b^\dagger b)\ , \tag{5.25}$$

that satisfy the $SU(2)$ algebraic relations $[J_x\,,\,J_y] = i\,J_z$ and their cyclic permutations. They are all non-local with respect to the algebraic bipartition $(\mathcal{A},\mathcal{B})$, because they cannot be factorized as $J_i = A_i B_i$ ($A_i \in \mathcal{A}$, $B_i \in \mathcal{B}$), and such are the rotations $e^{i\theta J_x}$ and $e^{i\theta J_y}$ they generate, while $e^{i\theta J_z} = e^{i\theta a^\dagger a} e^{-i\theta b^\dagger b}$ is $(\mathcal{A},\mathcal{B})$-local.

By means of the Bogolubov transformation (5.20) one rewrites

$$J_x = \frac{1}{2}(c^\dagger c - d^\dagger d)\ ,\ J_y = \frac{1}{2i}(d^\dagger c - d c^\dagger)\ ,\ J_z = \frac{1}{2}(c^\dagger d + c d^\dagger)\ . \tag{5.26}$$

Relatively to $(\mathcal{C},\mathcal{D})$, it is now $e^{i\theta\,J_x} = e^{i\theta\,c^\dagger c} e^{-i\theta\,d^\dagger d}$ which acts locally.

5.1.2. Two-mode N bosons and noise

An important feature of matter interferometry based upon ultracold atoms trapped in double-well potential is the coherence between the spatial modes; this is endangered by the presence of a dephasing noise that tends to suppress the off-diagonal matrix elements $\rho_{k\ell} = {}_{\mathcal{AB}}\langle k, N-k\,|\,\rho\,|\,\ell, N-\ell\rangle_{\mathcal{AB}}$, $k \neq \ell$, with respect to the orthonormal basis of Fock states (5.8). The effects of this kind of noise can be described by the following Master Equation [2]

$$\partial_t \rho(t) = \gamma\Big(J_z\,\rho(t)\,J_z\, -\, \frac{1}{2}\{J_z^2\,,\,\rho(t)\}\Big), \tag{5.27}$$

where ρ is the N boson density matrix, γ measures the strength of the noise and J_z is the collective spin operator in (5.25) that commutes with the number operator $a^\dagger\,a + b^\dagger\,b$. One easily checks that the matrix elements with respect to the eigenstates (5.8) satisfy

$$\partial_t \rho_{k\ell}(t) = -\frac{\gamma}{2}(k-\ell)^2\,\rho_{k\ell}\ , \tag{5.28}$$

[2]This Master Equation is standard in the theory of open quantum systems; for details see Refs. [1, 7, 16, 77, 78]. For more recent applications to trapped ultracold gases, *e.g.* see Ref. [79–85].

whence this kind of noisy irreversible time-evolution tends to diagonalize the system states with respect to their basis:

$$\rho(t) = \sum_{k\ell=0}^{N} e^{-t\gamma(k-\ell)^2/2}\, \rho_{k\ell}\, |k, N-k\rangle_{\mathcal{AB}}\langle \ell, N-\ell| \ . \tag{5.29}$$

It thus follows that the $(\mathcal{A}, \mathcal{B})$-negativity either decreases exponentially in time,

$$\mathcal{N}_{\mathcal{A},\mathcal{B}}(\rho(t)) = \sum_{k\neq\ell} e^{-t\gamma(k-\ell)^2/2}\, |\rho_{k\ell}| \leq e^{-t\gamma/2}\, \mathcal{N}_{\mathcal{A},\mathcal{B}}(\rho) \ , \tag{5.30}$$

if the initial state is $(\mathcal{A}, \mathcal{B})$-entangled, or remains zero as the dephasing noise has no possibility of creating non-local effects with respect to the bipartition $(\mathcal{A}, \mathcal{B})$. This is best seen by rewriting the solution (5.29) in the more suggestive form

$$\rho(t) = \frac{1}{2\sqrt{\pi}} \int_{-\infty}^{+\infty} \mathrm{d}u\, e^{-u^2/4}\, e^{-i\sqrt{t\gamma/2}\, u\, J_z}\, \rho\, e^{+i\sqrt{t\gamma/2}\, u\, J_z}, \tag{5.31}$$

which, on one hand, explicitly exhibits the Kraus form (2.25) of the completely positive maps solutions to (5.28) and, on the other hand, shows the impossibility of generating $(\mathcal{A}, \mathcal{B})$-entanglement as the rotations generated by J_z are all $(\mathcal{A}, \mathcal{B})$-local.

However, they are not local with respect to the bipartition $(\mathcal{C}, \mathcal{D})$ obtained by the Bogolubov transformation (5.20) and are thus able to raise from zero the $(\mathcal{C}, \mathcal{D})$-negativity of an initial $(\mathcal{C}, \mathcal{D})$-separable state. For instance, consider the pure state (5.23) as initial state. Using (5.20) one finds

$$e^{-i\beta J_z} |N, 0\rangle_{\mathcal{CD}} = \frac{1}{\sqrt{N!}} \Big(\frac{a^\dagger e^{-i\beta/2} + b^\dagger e^{i\beta/2}}{\sqrt{2}}\Big)^N |0\rangle = \Big| \cos^2 \beta/2, \pi/2 \Big\rangle_{\mathcal{CD}}, \tag{5.32}$$

so that the time-evolving state reads

$$\rho(t) = \frac{1}{2\sqrt{\pi}} \int_{-\infty}^{+\infty} \mathrm{d}u\, e^{-u^2/4} \Big|\ cos^2(u\sqrt{t\gamma/2}), \pi/2 \Big\rangle_{\mathcal{CD}} \Big\langle \cos^2(u\sqrt{t\gamma/2}), \pi/2 \Big|. \tag{5.33}$$

The time-evolution thus results in a mixed state which surely has non-vanishing off-diagonal elements

$$\begin{aligned} {}_{\mathcal{CD}}\langle k, N-k|\rho(t)|\ell, N-\ell\rangle_{\mathcal{CD}} = \frac{1}{\sqrt{\pi}} \int_0^{+\infty} \mathrm{d}u\, e^{-u^2/4} \sqrt{\binom{N}{k}\binom{N}{\ell}}\ \times \\ \times \cos^{k+\ell}\left(u\sqrt{\frac{t\gamma}{2}}\right) \sin^{2N-k-\ell}\left(u\sqrt{\frac{t\gamma}{2}}\right) e^{-i\pi/4(k-\ell)}, \end{aligned}$$

with respect to the orthonormal basis of eigenstates of $c^\dagger c + d^\dagger d$ and thus $\mathcal{N}_{\mathcal{CD}}(\rho(t)) > 0$.

5.2. Metrology and entanglement

The use of N bosons states for measuring an angle θ by interferometric techniques is based on the following scheme: an input state ρ is rotated by θ into a final state

$$\rho_\theta = e^{-i\theta J_{\boldsymbol{n}_1}}\,\rho\, e^{i\theta J_{\boldsymbol{n}_1}}\,, \tag{5.34}$$

by means of the collective spin operator in the direction of a unit vector $\boldsymbol{n}_1$: $J_{\boldsymbol{n}_1} = \boldsymbol{n}_1 \cdot \boldsymbol{J}$; then, on the rotated state one performs the measurement of a collective spin operator $J_{\boldsymbol{n}_2}$, where $\boldsymbol{n}_2 \perp \boldsymbol{n}_1$ and, for sake of convenience, we choose ρ such that $\langle J_{\boldsymbol{n}_3}\rangle = \mathrm{Tr}(\rho\, J_{\boldsymbol{n}_3}) \neq 0$ along the third orthogonal unit vector $\boldsymbol{n}_3$. By error propagation, the mean square error $\Delta J_{\boldsymbol{n}_2} = \sqrt{\left\langle J^2_{\boldsymbol{n}_2}\right\rangle - \langle J_{\boldsymbol{n}_2}\rangle^2}$ is related to the error $\delta\theta$ in the measurement of the small rotation angle θ by [41]:

$$\delta^2\theta = \frac{\Delta^2 J_{\boldsymbol{n}_2}}{\left(\partial_\theta \left\langle J_{\boldsymbol{n}_2}\right\rangle_{\theta_{|\theta=0}}\right)^2} = \frac{\Delta^2 J_{\boldsymbol{n}_2}}{\left\langle J_{\boldsymbol{n}_3}\right\rangle^2} = \frac{\xi_W^2}{N}, \tag{5.35}$$

where the parameter

$$\xi_W^2 := \frac{N\Delta^2 J_{\boldsymbol{n}_2}}{\left\langle J_{\boldsymbol{n}_3}\right\rangle^2}, \tag{5.36}$$

measure the amount of *squeezing* in the state ρ. Indeed, for any orthogonal triplet of space-directions $\boldsymbol{n}_1$, $\boldsymbol{n}_2$, $\boldsymbol{n}_3$, the Heisenberg uncertainty relations read

$$\Delta^2 Jq_{\boldsymbol{n}_1}\Delta^2 J_{\boldsymbol{n}_2} \geqslant \frac{1}{4}\left\langle J_{\boldsymbol{n}_3}\right\rangle^2, \tag{5.37}$$

and ρ is a *squeezed* state if one of the variances can be made smaller than $\frac{1}{2}\left|\left\langle J_{\boldsymbol{n}_3}\right\rangle\right|$.

The value $\delta^2\theta = 1/N$ is called shot-noise limit; in the case of distinguishable qubits, it gives the lower bound to the attainable accuracies when the input state ρ is separable [46]. Therefore, for systems consisting of distinguishable qubits, entanglement in the initial state ρ is necessary to achieve sub-shot-noise accuracies. An entangled initial state is usually prepared by preliminary squeezing operations [55, 56]; indeed, from (5.35), preparing the initial state ρ such that $\xi_W^2 < 1$ guarantees an achievable sub-shot-noise accuracy in the determination of θ. However, in Ref. [58] it is shown that this is not strictly necessary in ultracold atom interferometry; indeed, in such experimental contexts, one is dealing with identical bosons and then the necessary non-local effects necessary for beating the shot-noise limit can be provided by the interferometric apparatus itself.

In the previous section we have seen that the presence of dephasing noise destroys $(\mathcal{AB})$-entanglement, but creates $(\mathcal{CD})$-entanglement. It is thus of interest to see whether this latter fact allows one to achieve sub-shot-noise accuracies by simply letting the $(\mathcal{CD})$-non-local noisy mechanism act. In order to do so we need compute the mean values

$\langle J_{\boldsymbol{n}}\rangle_t$ and $\langle J^2_{\boldsymbol{n}}\rangle_t$ of collective spin operator aligned along the unit vector $\boldsymbol{n}$ with respect to the time-evolving state (5.29); use of (5.31) yields

$$\langle J_{\boldsymbol{n}}\rangle_t = \frac{1}{2\sqrt{\pi}}\int_{-\infty}^{+\infty} \mathrm{d}u\, e^{-u^2/4}\,\mathrm{Tr}(\rho\, J_{\boldsymbol{n}(u,t)}), \tag{5.38}$$

in terms of the rotated unit vector

$$\boldsymbol{n}(u,t) = \begin{pmatrix} \cos\left(u\sqrt{\frac{t\gamma}{2}}\right) & \sin\left(u\sqrt{\frac{t\gamma}{2}}\right) & 0 \\ -\sin\left(u\sqrt{\frac{t\gamma}{2}}\right) & \cos\left(u\sqrt{\frac{t\gamma}{2}}\right) & 0 \\ 0 & 0 & 1 \end{pmatrix} \boldsymbol{n}\ . \tag{5.39}$$

Furthermore, given the mean value

$$\left\langle J^2_{\boldsymbol{n}}\right\rangle_t = \frac{1}{2\sqrt{\pi}}\int_{-\infty}^{+\infty} \mathrm{d}u\, e^{-u^2/4}\,\mathrm{Tr}(\rho\, J^2_{\boldsymbol{n}(u,t)}), \tag{5.40}$$

one finds

$$\begin{aligned}\Delta^2_t J_{\boldsymbol{n}} = \left\langle J^2_{\boldsymbol{n}}\right\rangle_t - \langle J_{\boldsymbol{n}}\rangle^2_t = \frac{1}{2\sqrt{\pi}}\int_{-\infty}^{+\infty} \mathrm{d}u\, e^{-u^2/4}\,\Delta^2 J_{\boldsymbol{n}(u,t)}\ + \\ + \frac{1}{2\sqrt{\pi}}\int_{-\infty}^{+\infty} \mathrm{d}u\, e^{-u^2/4}\left(\mathrm{Tr}(\rho\, J_{\boldsymbol{n}(u,t)})\right)^2 - \left(\frac{1}{2\sqrt{\pi}}\int_{-\infty}^{+\infty} \mathrm{d}u\, e^{-u^2/4}\,\mathrm{Tr}(\rho\, J_{\boldsymbol{n}(u,t)})\right)^2 .\end{aligned}$$

Because of the convexity of the function $f(x) = x^2$, the second line above is positive and one estimates

$$\Delta^2_t J_{\boldsymbol{n}} = \left\langle J^2_{\boldsymbol{n}}\right\rangle_t - \langle J_{\boldsymbol{n}}\rangle^2_t \ \geq\ \frac{1}{2\sqrt{\pi}}\int_{-\infty}^{+\infty} \mathrm{d}u\, e^{-u^2/4}\,\Delta^2 J_{\boldsymbol{n}(u,t)}. \tag{5.41}$$

If the initial state ρ is such that for no orthogonal directions $\boldsymbol{n}_{2,3}$ the squeezing parameter (5.36) is less than one, then, as $\boldsymbol{n}_2(u,t) \perp \boldsymbol{n}_3(u,t)$, one gets

$$\frac{1}{2\sqrt{\pi}}\int_{-\infty}^{+\infty} \mathrm{d}u\, e^{-u^2/4}\,\Delta^2 J_{\boldsymbol{n}_2(u,t)} \geq \frac{1}{N}\frac{1}{2\sqrt{\pi}}\int_{-\infty}^{+\infty} \mathrm{d}u\, e^{-u^2/4}\,\left\langle J_{\boldsymbol{n}_3(u,t)}\right\rangle^2, \tag{5.42}$$

and, again by convexity,

$$\begin{aligned}\frac{1}{N}\frac{1}{2\sqrt{\pi}}\int_{-\infty}^{+\infty} \mathrm{d}u\, e^{-u^2/4}\,\left\langle J_{\boldsymbol{n}_3(u,t)}\right\rangle^2 \ &\geq\ \frac{1}{N}\left(\frac{1}{2\sqrt{\pi}}\int_{-\infty}^{+\infty} \mathrm{d}u\, e^{-u^2/4}\,\left\langle J_{\boldsymbol{n}_3(u,t)}\right\rangle\right)^2 \\ &=\ \frac{1}{N}\,\langle J_{\boldsymbol{n}_3}\rangle^2_t\,.\end{aligned}$$

Thus, although under the dephasing noise some N-bosons states can get entangled, no squeezing can be achieved by such means; indeed,

$$\frac{N\Delta_t^2 J_{\boldsymbol{n}_2}}{\langle J_{\boldsymbol{n}_3}\rangle_t^2} \geq 1. \tag{5.43}$$

Though not metrologically relevant, such an environment generated entanglement might however be useful for other quantum informational tasks like those involving quantum gates constructed by using systems of ultracold bosons trapped in optical lattices [85].

5.3. Conclusions

We have seen that when dealing with a system of identical bosons it is necessary to introduce a new, algebraic definition of separability; indeed, the standard one based on an a priori factorized form of the involved Hilbert space is no longer available. A natural notion of entanglement given in terms of correlations among commuting subalgebras of observables can be defined. With respect to this notion of entanglement, unlike what happens for distinguishable qubits, entangled states of N bosonic qubits are completely identified by their non-zero negativity which is therefore an exhaustive bipartite entanglement witness for such systems. Furthermore, we have showed that even a simple dephasing noise which, for distinguishable particles exhibits merely decoherence effects, can instead generate entanglement among identical bosons. These results may be relevant in concrete applications to systems of ultracold atoms trapped in optical lattices; however, while the entanglement generated by purely dephasing noise can be used for the practical implementation of quantum informational protocols, it cannot augment the sensitivity of ultracold atom based interferometric devices.

Appendix A.

Complementary material

A.1. Nakajima-Zwanzig Equation

Here we derive explicitly eq. (2.54), known in literature as *Nakajima-Zwanzig equation*, using the projectors $\mathbf{P}$ and $\mathbf{Q}$

$$\mathbf{P}\rho_{S+E} \equiv \mathrm{Tr_E}[\rho_{S+E}] \otimes \rho_E$$
$$\mathbf{Q} \equiv \mathbf{1}_{S+E} - \mathbf{P}$$

and the relations

$$\mathbf{L}_E[\rho_E] = 0 \tag{A.1}$$
$$\mathrm{Tr_E}(R_\alpha \rho_E) = 0. \tag{A.2}$$

First of all we start from the expression of the total Hamiltonian of the system and environment:

$$H_S \otimes \mathbf{1}_E + \mathbf{1}_S \otimes H_E + \lambda \sum_\alpha S_\alpha \otimes R_\alpha \tag{A.3}$$

Then we work out the following expressions from (2.52)

$$\begin{aligned}
\mathbf{L}^{\lambda PP}_{S+E}\left[\rho_S(t) \otimes \rho_E\right] &= \mathbf{P} \circ \mathbf{L}_{S+E}\left[\rho_S(t) \otimes \rho_E\right] = \\
&= \mathbf{P}\left[-i[H_S, \rho_S(t)] \otimes \rho_E\right] + \mathbf{P}\left[-i\rho_S(t) \otimes [H_E, \rho_E]\right] + \\
&+ \mathbf{P}\Big[-i\lambda \sum_\alpha S_\alpha \otimes R_\alpha, \rho_S(t) \otimes \rho_E\Big] = \\
&= -i[H_S, \rho_S(t)] \otimes \rho_E - i\lambda \sum_\alpha [S_\alpha, \rho_S(t)]\,\mathrm{Tr_E}(R_\alpha \rho_E) \otimes \rho_E = \\
&= -i[H_S, \rho_S(t)] \otimes \rho_E = \\
&= \mathbf{L}_S[\rho_S(t)] \otimes \rho_E
\end{aligned} \tag{A.4}$$

$$\mathbf{L}^{\lambda\,PQ}_{S+E}[\rho_{S+E}] = \big(\mathrm{Tr_E}(\mathbf{L}^{\lambda}_{S+E}[\rho_{S+E}]) - \mathrm{Tr_E}\big(\mathbf{L}^{\lambda}_{S+E}[\mathrm{Tr_E}\rho_{S+E}\otimes\rho_E]\big)\big)\otimes\rho_E \tag{A.5}$$

We calculate the second term

$$\begin{aligned}
\mathrm{Tr_E}\big(\mathbf{L}^{\lambda}_{S+E}[\mathrm{Tr_E}\rho_{S+E}\otimes\rho_E]\big) &= -i\mathrm{Tr_E}[H_S\otimes\mathbf{1}_E, \mathrm{Tr_E}\rho_{S+E}\otimes\rho_E] - i\mathrm{Tr_E}[\mathbf{1}_S\otimes H_E, \mathrm{Tr_E}\rho_{S+E}\otimes\rho_E]+\\
&- i\lambda\mathrm{Tr_E}\left[\sum_\alpha S_\alpha\otimes R_\alpha\,,\ \mathrm{Tr_E}\rho_{S+E}\otimes\rho_E\right] =\\
&= -i[H_S, \mathrm{Tr_E}\rho_{S+E}] - i\lambda\sum_\alpha[S_\alpha, \mathrm{Tr_E}\rho_{S+E}]\,\mathrm{Tr_E}(R_\alpha\rho_E) =\\
&= -i[H_S, \mathrm{Tr_E}\rho_{S+E}]
\end{aligned} \tag{A.6}$$

and then the first

$$\mathrm{Tr_E}(\mathbf{L}^{\lambda}_{S+E}[\rho_{S+E}]) = -i\mathrm{Tr_E}\left([H_S\otimes\mathbf{1}_E, \rho_{S+E}] + [\mathbf{1}_S\otimes H_E, \rho_{S+E}] + \lambda\sum_\alpha[S_\alpha\otimes R_\alpha, \rho_{S+E}]\right) \tag{A.7}$$

We use an o.n.b. $\{|\sigma\rangle\otimes|\epsilon\rangle\}_{\sigma,\epsilon}\in\mathcal{H}_S\otimes\mathcal{H}_E$ made up of the eigenvectors of the two Hamiltonians H_S and H_E: $H_S = \sum_\sigma|\sigma\rangle\,E_\sigma\,\langle\sigma|$, $H_E = \sum_\epsilon|\epsilon\rangle\,\epsilon\,\langle\epsilon|$ and the first term of (A.7) becomes, expanding the Hamiltonians into their eigenbases,

$$\begin{aligned}
-i\mathrm{Tr_E}[H_S\otimes\mathbf{1}_E, \rho_{S+E}]_{\sigma\tau} &= -i\sum_\epsilon\langle\sigma|\otimes\langle\epsilon|\,H_S\otimes\mathbf{1}_E\cdot\rho_{S+E} - \rho_{S+E}\cdot H_S\otimes\mathbf{1}_E\,|\tau\rangle\otimes|\epsilon\rangle =\\
&- i\sum_{\epsilon,\mu}\langle\sigma|\otimes\langle\epsilon|\,|\mu\rangle\,E_\mu\,\langle\mu|\otimes\mathbf{1}_E\cdot\rho_{S+E}\,|\tau\rangle\otimes|\epsilon\rangle+\\
&+ i\sum_{\epsilon,\mu}\langle\sigma|\otimes\langle\epsilon|\,\rho_{S+E}\cdot|\mu\rangle\,E_\mu\,\langle\mu|\otimes\mathbf{1}_E\,|\tau\rangle\otimes|\epsilon\rangle =\\
&= -i\sum_{\epsilon,\mu}(\delta_{\sigma\mu}E_\mu\,\langle\mu|\otimes\langle\epsilon|\,\rho_{S+E}\,|\tau\rangle\otimes|\epsilon\rangle+\\
&\qquad -\delta_{\mu\tau}E_\mu\,\langle\sigma|\otimes\langle\epsilon|\,\rho_{S+E}\,|\mu\rangle\otimes|\epsilon\rangle) =\\
&- i\sum_\epsilon\left(E_\sigma\,\langle\sigma|\,\langle\epsilon|\,\rho_{S+E}\,|\tau\rangle\,|\epsilon\rangle - E_\tau\,\langle\sigma|\,\langle\epsilon|\,\rho_{S+E}\,|\tau\rangle\,|\epsilon\rangle\right) =\\
&= -i\,[H_S, \mathrm{Tr_E}\rho_{S+E}]_{\sigma\tau}
\end{aligned} \tag{A.8}$$

By the same method we get for the second term in (A.7)

$$
\begin{aligned}
-i\mathrm{Tr_E}[\mathbf{1}_S\otimes H_E,\rho_{S+E}]_{\sigma\tau} &= -i\sum_{\epsilon}\left(\langle\sigma|\,\langle\epsilon|\,\mathbf{1}_S\otimes H_E\cdot\rho_{S+E}-\rho_{S+E}\cdot\mathbf{1}_S\otimes H_E\,|\tau\rangle\,|\epsilon\rangle\right) = \\
&= -i\sum_{\epsilon,\nu}\langle\sigma|\,\langle\epsilon|\,\mathbf{1}_S\otimes|\nu\rangle\,\nu\,\langle\nu|\cdot\rho_{S+E}\,|\tau\rangle\,|\epsilon\rangle + \\
&\quad + i\sum_{\epsilon,\nu}\langle\sigma|\,\langle\epsilon|\,\rho_{S+E}\cdot\mathbf{1}_S\otimes|\nu\rangle\,\nu\,\langle\nu|\,|\tau\rangle\,|\epsilon\rangle = \\
&= -i\sum_{\epsilon}\epsilon\,\langle\sigma|\,\langle\epsilon|\,\rho_{S+E}\,|\tau\rangle\,|\epsilon\rangle + i\sum_{\epsilon}\epsilon\,\langle\sigma|\,\langle\epsilon|\,\rho_{S+E}\,|\tau\rangle\,|\epsilon\rangle = \\
&= 0
\end{aligned}
\tag{A.9}
$$

Collecting (A.8) and (A.9) and subtracting (A.7) from (A.6) we arrive at

$$
\begin{aligned}
\mathbf{L}^{\lambda PQ}_{S+E}[\rho_{S+E}] &= -i\lambda\sum_{\alpha}\mathrm{Tr_E}[S_\alpha\otimes R_\alpha,\rho_{S+E}]\otimes\rho_E = \\
&= \lambda\mathbf{P}\circ\mathbf{L}'[\rho_{S+E}] = \\
&= \lambda\mathbf{P}\circ\mathbf{L}'\circ(\mathbf{P}+\mathbf{Q})[\rho_{S+E}] = \\
&= \lambda\mathbf{P}\circ\mathbf{L}'\circ\mathbf{Q}[\rho_{S+E}]
\end{aligned}
\tag{A.10}
$$

because $\mathbf{P}\circ\mathbf{L}'\circ\mathbf{P}[\rho_{S+E}]=0$ as we have seen in the last passage of (A.6).

$\mathbf{L}^{\lambda QP}_{S+E}[\rho_S(s)\otimes\rho_E]$ is rather simple:

$$
\begin{aligned}
\mathbf{L}^{\lambda QP}_{S+E}[\rho_S(s)\otimes\rho_E] &= (\mathbf{1}-\mathbf{P})\circ\mathbf{L}_{S+E}\circ\mathbf{P}[\rho_S(s)\otimes\rho_E] = \\
&= \mathbf{L}^{\lambda}_{S+E}[\rho_S(s)\otimes\rho_E]-\mathbf{P}\circ L_{S+E}[\rho_S(s)\otimes\rho_E] = \\
&= -i[H_S,\rho_S(s)]\otimes\rho_E-i\rho_S(s)\otimes[H_E,\rho_E]-i\lambda\sum_{\alpha}[S_\alpha\otimes R_\alpha,\rho_S(s)\otimes\rho_E]+ \\
&\quad -\Big(-i[H_S,\rho_S(s)]\otimes\rho_E-i\lambda\sum_{\alpha}[S_\alpha,\rho_S(s)]\,\mathrm{Tr_E}(R_\alpha\rho_E)\otimes\rho_E\Big) = \\
&= +\lambda\mathbf{L}'[\rho_S(s)\otimes\rho_E]
\end{aligned}
\tag{A.11}
$$

Finally, eqs. (A.6), (A.10) and (A.11) allow us, starting from (2.52) and tracing out the environment degrees of freedom, to write down the generalized Master Equation in the form (2.54):

$$
\partial_t\rho_S(t)=\mathbf{L}_S[\rho_S(t)]+\lambda^2\int_0^t \mathrm{d}s\mathrm{Tr_E}\Big(\mathbf{L}'\circ e^{(t-s)\mathbf{L}^{QQ}_{S+E}}\circ\mathbf{L}'[\rho_S(s)\otimes\rho_E]\Big) \tag{A.12}
$$

A.2. Davies's Master Equation

In this section we find an explicit expression of the generator $\mathbf{K}_3$ (eq. (2.67)) in the Kossakowski-Lindblad form and we show that the related dynamics is completely positive.

Starting from (2.66), we have

$$\mathbf{K}_3[\rho] = \lim_{T\to\infty} \frac{1}{2T}\int_{-T}^{T} \mathrm{d}t\, e^{-t\mathbf{L}_S} K_2 e^{t\mathbf{L}_S}\rho = \tag{A.13}$$

$$= \lim_{T\to\infty} \frac{1}{2T}\int_{-T}^{T} \mathrm{d}t\, e^{-t\mathbf{L}_S}\int_0^{+\infty}\mathrm{d}v\, e^{-v\mathbf{L}_S}\mathrm{Tr_E}\big(\mathbf{L}'\circ e^{v(\mathbf{L}_S+\mathbf{L}_E)}\circ \mathbf{L}'[e^{t\mathbf{L}_S}\rho\otimes\rho_E]\big) \tag{A.14}$$

We work out every argument in the formula above, starting from the inner and proceding outwards. Thus:

$$\mathbf{L}'[e^{t\mathbf{L}_S}\rho\otimes\rho_E] = -i\sum_\alpha \big(S_\alpha e^{t\mathbf{L}_S}[\rho]\otimes R_\alpha\rho_E - e^{t\mathbf{L}_S}[\rho]S_\alpha\otimes\rho_E R_\alpha\big) \tag{A.15}$$

The action of the unitary operator $e^{t\mathbf{L}_S}$ on the operators S_α

$$e^{v\mathbf{L}_S}[S_\alpha] = e^{-ivH_S}[S_\alpha]e^{ivH_S} \equiv S_\alpha(-v) \tag{A.16}$$

corresponds, up to a minus, to the switch from the Schrödinger to the Interaction Picture

$$S_\alpha(t) \equiv e^{itH_S}S_\alpha e^{-itH_S}. \tag{A.17}$$

The same for $e^{t\mathbf{L}_E}$ and the operators R_α.

Therefore we have

$$e^{v(\mathbf{L}_S+\mathbf{L}_E)}\circ\mathbf{L}'[e^{t\mathbf{L}_S}\rho\otimes\rho_E] =$$
$$= -i\sum_\alpha\big(S_\alpha(-v)e^{(t+v)\mathbf{L_S}}[\rho]\otimes R_\alpha(-v)\rho_E - e^{(t+v)\mathbf{L}_S}[\rho]S_\alpha(-v)\otimes\rho_E R_\alpha(-v)\big)\,, \tag{A.18}$$

and

$$\mathbf{L}'\circ e^{v(\mathbf{L}_S+\mathbf{L}_E)}\circ\mathbf{L}'[e^{t\mathbf{L}_S}\rho\otimes\rho_E] =$$
$$= -\sum_{\beta,\alpha}\big(S_\beta S_\alpha(-v)e^{(t+v)\mathbf{L_S}}[\rho]\otimes R_\beta R_\alpha(-v)\rho_E - S_\alpha(-v)e^{(t+v)\mathbf{L_S}}[\rho]S_\beta\otimes R_\alpha(-v)\rho_E R_\beta +$$
$$-S_\beta e^{(t+v)\mathbf{L}_S}[\rho]S_\alpha(-v)\otimes R_\beta\rho_E R_\alpha(-v) + e^{(t+v)\mathbf{L}_S}[\rho]S_\alpha(-v)S_\beta\otimes\rho_E R_\alpha(-v)R_\beta\big)\,. \tag{A.19}$$

In order to calculate the trace over E we define the two-point correlation functions

$$F_{\beta\alpha}(v) \equiv \langle R_\beta R_\alpha(-v) \rangle = \mathrm{Tr_E}(R_\beta R_\alpha(-v)\rho_E), \tag{A.20}$$

having the following property

$$\begin{aligned} F_{\alpha\beta}(-v) &\equiv \mathrm{Tr_E}(R_\alpha R_\beta(v)\rho_E) = \mathrm{Tr_E}(e^{-iH_E v} R_\alpha e^{iH_E v} R_\beta e^{-iH_E v}\rho_E e^{iH_E v}) = \\ &= \mathrm{Tr_E}(R_\alpha(-v) R_\beta \rho_E) = \mathrm{Tr_E}(\rho_E R_\alpha(-v) R_\beta) = (\mathrm{Tr_E}(R_\beta R_\alpha(-v)\rho_E))^* = \\ &= F_{\beta\alpha}(v)^*. \end{aligned} \tag{A.21}$$

Consequently we can write

$$\begin{aligned} &\mathrm{Tr_E}(\mathbf{L}' \circ e^{v(\mathbf{L}_S+\mathbf{L}_E)} \circ \mathbf{L}'[e^{t\mathbf{L}_S}\rho \otimes \rho_E]) = \\ &= -\sum_{\beta,\alpha} \big(S_\beta S_\alpha(-v) e^{(t+v)\mathbf{L}_S}[\rho] F_{\beta\alpha}(v) - S_\alpha(-v) e^{(t+v)\mathbf{L}_S}[\rho] S_\beta F_{\beta\alpha}(v) + \\ &\quad - S_\beta e^{(t+v)\mathbf{L}_S}[\rho] S_\alpha(-v) F_{\alpha\beta}(-v) + e^{(t+v)\mathbf{L}_S}[\rho] S_\alpha(-v) S_\beta F_{\alpha\beta}(-v)\big)\,. \end{aligned} \tag{A.22}$$

Proceding further we get

$$\begin{aligned} &e^{-v\mathbf{L}_S}\mathrm{Tr_E}(\mathbf{L}' \circ e^{v(\mathbf{L}_S+\mathbf{L}_E)} \circ \mathbf{L}'[e^{t\mathbf{L}_S}\rho \otimes \rho_E]) = \\ &= -\sum_{\beta,\alpha} \big(S_\beta(v) S_\alpha e^{t\mathbf{L}_S}[\rho] F_{\beta\alpha}(v) - S_\alpha e^{t\mathbf{L}_S}[\rho] S_\beta(v) F_{\beta\alpha}(v) + \\ &\quad - S_\beta(v) e^{t\mathbf{L}_S}[\rho] S_\alpha F_{\alpha\beta}(-v) + e^{t\mathbf{L}_S}[\rho] S_\alpha S_\beta(v) F_{\alpha\beta}(-v)\big)\,, \end{aligned} \tag{A.23}$$

and

$$\begin{aligned} &e^{-t\mathbf{L}_S}\int_0^{+\infty} \mathrm{d}v\, e^{-v\mathbf{L}_S}\mathrm{Tr_E}(\mathbf{L}' \circ e^{v(\mathbf{L}_S+\mathbf{L}_E)} \circ \mathbf{L}'[e^{t\mathbf{L}_S}\rho \otimes \rho_E]) = \\ &= -\sum_{\beta,\alpha}\int_0^{+\infty} \mathrm{d}v\ (S_\beta(t+v) S_\alpha(t)\rho F_{\beta\alpha}(v) - S_\alpha(t)\rho S_\beta(t+v) F_{\beta\alpha}(v) + \\ &\quad - S_\beta(t+v)\rho S_\alpha(t) F_{\alpha\beta}(-v) + \rho S_\alpha(t) S_\beta(t+v) F_{\alpha\beta}(-v))\,. \end{aligned} \tag{A.24}$$

Finally the expression of the generator $\mathbf{K}_3$ will be given by the limit $T \to +\infty$ of

$$\begin{aligned} &\frac{1}{2T}\int_{-T}^{+T} \mathrm{d}t\, e^{-t\mathbf{L}_S}\int_0^{+\infty} \mathrm{d}v\, e^{-v\mathbf{L}_S}\mathrm{Tr_E}(\mathbf{L}' \circ e^{v(\mathbf{L}_S+\mathbf{L}_E)} \circ \mathbf{L}'[e^{t\mathbf{L}_S}\rho \otimes \rho_E]) = \\ &= -\frac{1}{2T}\sum_{\beta,\alpha}\int_{-T}^{+T}\mathrm{d}t\int_0^{+\infty}\mathrm{d}v\ (S_\beta(t+v)S_\alpha(t)\rho - S_\alpha(t)\rho S_\beta(t+v))\, F_{\beta\alpha}(v) + \mathrm{h.c.}\,. \end{aligned} \tag{A.25}$$

We can expand $S_\beta(t+v)$ and $S_\alpha(t)$ in Fourier series:

$$\begin{aligned} S_\beta(t+v) &= \sum_\omega e^{i\omega(t+v)} S_\beta(\omega) \\ S_\alpha(t) &= \sum_{\omega'} e^{i\omega' t} S_\alpha(\omega'). \end{aligned} \tag{A.26}$$

So we have for (A.25)

$$\frac{1}{2T} \sum_{\beta,\alpha} \sum_{\omega,\omega'} \int_{-T}^{+T} \mathrm{d}t \int_0^{+\infty} \mathrm{d}v\, F_{\beta\alpha}(v) \left(S_\alpha(\omega')\rho S_\beta(\omega) - S_\beta(\omega) S_\alpha(\omega')\rho\right) e^{iv\omega} e^{it(\omega+\omega')} + \text{h.c.}\,. \tag{A.27}$$

Taking the limit $T \to +\infty$ the integration $\frac{1}{2T}\int_{-T}^{+T} \mathrm{d}t\, e^{i(\omega+\omega')t}$ gives a $\delta(\omega+\omega')$ and we can write

$$\begin{aligned} &\sum_{\beta,\alpha} \sum_\omega \int_0^{+\infty} \mathrm{d}v\, F_{\beta\alpha}(v) \left(S_\alpha(-\omega)\rho S_\beta(\omega) - S_\beta(\omega) S_\alpha(-\omega)\rho\right) e^{iv\omega} + \text{h.c.} = \\ &= \sum_{\beta,\alpha} \sum_\omega \int_0^{+\infty} \mathrm{d}v\, F_{\beta\alpha}(v) \left(S_\alpha^\dagger(\omega)\rho S_\beta(\omega) - S_\beta(\omega) S_\alpha^\dagger(\omega)\rho\right) e^{iv\omega} + \text{h.c.}\,, \end{aligned} \tag{A.28}$$

since $S_\alpha(-\omega) = S_\alpha^\dagger(\omega)$.

The hermitian conjugate of the above expression is

$$\begin{aligned} &\sum_{\beta,\alpha} \sum_\omega \int_0^{+\infty} \mathrm{d}v\, F_{\alpha\beta}(-v) \left(S_\beta^\dagger(\omega)\rho S_\alpha(\omega) - \rho S_\alpha(\omega) S_\beta^\dagger(\omega)\right) e^{-iv\omega} = \\ &= \sum_{\beta,\alpha} \sum_\omega \int_{-\infty}^{0} \mathrm{d}v\, F_{\alpha\beta}(v) \left(S_\beta^\dagger(\omega)\rho S_\alpha(\omega) - \rho S_\alpha(\omega) S_\beta^\dagger(\omega)\right) e^{iv\omega} = \\ &= \sum_{\beta,\alpha} \sum_\omega \int_{-\infty}^{0} \mathrm{d}v\, F_{\beta\alpha}(v) \left(S_\alpha^\dagger(\omega)\rho S_\beta(\omega) - \rho S_\beta(\omega) S_\alpha^\dagger(\omega)\right) e^{iv\omega}, \end{aligned} \tag{A.29}$$

where we have made a change of integration variable in the first passage and swapped α and β indices in the second.

So we can write the expression

$$\lim_{T\to+\infty}\frac{1}{2T}\int_{-T}^{+T}\mathrm{d}t\, e^{-t\mathbf{L}_S}\int_0^{+\infty}\mathrm{d}v\, e^{-v\mathbf{L}_S}\mathrm{Tr}_{\mathrm{E}}(\mathbf{L}'\circ e^{v(\mathbf{L}_S+\mathbf{L}_E)}\circ\mathbf{L}'[e^{t\mathbf{L}_S}\rho\otimes\rho_E])=$$
$$=\sum_{\beta,\alpha}\sum_{\omega}\left(\int_{-\infty}^{+\infty}\mathrm{d}v\, F_{\beta\alpha}(v)S^{\dagger}_{\alpha}(\omega)\rho S_{\beta}(\omega)e^{iv\omega}-\int_0^{+\infty}\mathrm{d}v\, F_{\beta\alpha}(v)S_{\beta}(\omega)S^{\dagger}_{\alpha}(\omega)\rho e^{iv\omega}+\right.$$
$$\left.-\int_{-\infty}^{0}\mathrm{d}v\, F_{\beta\alpha}(v)\rho S_{\beta}(\omega)S^{\dagger}_{\alpha}(\omega)e^{iv\omega}\right). \quad \text{(A.30)}$$

The first integral is just the Fourier transform of $F_{\beta\alpha}$:

$$\hat{F}_{\beta\alpha}(-\omega)=\int_{-\infty}^{+\infty}\mathrm{d}v\, e^{-iv(-\omega)}F_{\beta\alpha}(v). \quad \text{(A.31)}$$

Introducing the Heaviside step function

$$H(v)=\begin{cases}1 & v\in[0,+\infty];\\ 0 & v\in[-\infty,0[,\end{cases} \quad \text{(A.32)}$$

with Fourier transform

$$\hat{H}(\omega)=\left(\mathrm{p.v.}\frac{1}{ik}+\pi\delta(k)\right), \quad \text{(A.33)}$$

we can define $f_{\beta\alpha}(v)\equiv H(v)F_{\beta\alpha}(v)$ and in the second integral we can devise the Fourier transform of $f_{\beta\alpha}$:

$$\int_0^{+\infty}\mathrm{d}v\, F_{\beta\alpha}(v)e^{iv\omega}=\hat{f}_{\beta\alpha}(-\omega)=\widehat{H\cdot F_{\beta\alpha}}(-\omega)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}\mathrm{d}k\,\hat{H}(k)\hat{F}_{\beta\alpha}(-\omega-k)=$$
$$=\frac{1}{2\pi}\int_{-\infty}^{+\infty}\mathrm{d}k\left(\mathrm{p.v.}\frac{1}{ik}+\pi\delta(k)\right)\hat{F}_{\beta\alpha}(-\omega-k)=$$
$$=\frac{1}{2}\hat{F}_{\beta\alpha}(-\omega)-\frac{i}{2\pi}\mathrm{p.v.}\int_{-\infty}^{+\infty}\mathrm{d}k\,\frac{\hat{F}_{\beta\alpha}(-\omega-k)}{k}. \quad \text{(A.34)}$$

Here we have used the convolution integral to express the Fourier transform of the product $H\cdot F_{\beta\alpha}$.

Analogously:

$$\int_{-\infty}^{0} \mathrm{d}v F_{\beta\alpha}(v) e^{iv\omega} = \int_{-\infty}^{+\infty} \mathrm{d}v H(-v) F_{\beta\alpha}(v) e^{iv\omega} = \int_{-\infty}^{+\infty} \mathrm{d}v \, \underbrace{H(v) F_{\beta\alpha}(-v)}_{g_{\beta\alpha}(v)} \, e^{-iv\omega} =$$
$$= \hat{g_{\beta\alpha}}(\omega) = \widehat{H \cdot F^{(-)}_{\beta\alpha}}(\omega), \quad \text{(A.35)}$$

where $F^{(-)}_{\beta\alpha}(v) \equiv F_{\beta\alpha}(-v)$.

$$\Rightarrow \int_{-\infty}^{0} \mathrm{d}v \, F_{\beta\alpha}(v) e^{iv\omega} = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \mathrm{d}k \, \hat{H}(k) \hat{F}^{(-)}_{\beta\alpha}(\omega - k) = \int_{-\infty}^{+\infty} \frac{\mathrm{d}k}{2\pi} \, \hat{H}(k) \hat{F}_{\beta\alpha}(k - \omega) =$$
$$= \frac{1}{2} \hat{F}_{\beta\alpha}(-\omega) - \frac{i}{2\pi} \mathrm{p.v.} \int_{-\infty}^{+\infty} \mathrm{d}k \, \frac{\hat{F}_{\beta\alpha}(k-\omega)}{k}. \quad \text{(A.36)}$$

Summing the two "half-Fourier transforms" and (A.34) and (A.36):

$$- \left(\int_{0}^{+\infty} \mathrm{d}v \, F_{\beta\alpha}(v) e^{iv\omega} S_\beta(\omega) S^\dagger_\alpha(\omega) \rho + \int_{-\infty}^{0} \mathrm{d}v \, F_{\beta\alpha}(v) e^{iv\omega} \rho S_\beta(\omega) S^\dagger_\alpha(\omega) \right) =$$
$$= \frac{i}{2\pi} \int_{-\infty}^{+\infty} \mathrm{d}k \, \left(\frac{\hat{F}_{\beta\alpha}(-\omega - k)}{k} S_\beta(\omega) S^\dagger_\alpha(\omega) \rho + \frac{\hat{F}_{\beta\alpha}(-\omega + k)}{k} \rho S_\beta(\omega) S^\dagger_\alpha(\omega) \right) +$$
$$- \frac{\hat{F}_{\beta\alpha}(-\omega)}{2} \left(S_\beta(\omega) S^\dagger_\alpha(\omega) \rho + \rho S_\beta(\omega) S^\dagger_\alpha(\omega) \right). \quad \text{(A.37)}$$

In the end $\mathbf{K}_3[\rho]$ becomes:

$$\mathbf{K}_3[\rho] = \sum_\omega \sum_{\beta,\alpha} \hat{F}_{\beta\alpha}(-\omega) \left(S^\dagger_\alpha(\omega) \rho S_\beta(\omega) - \frac{1}{2} \left\{ S_\beta(\omega) S^\dagger_\alpha(\omega), \, \rho \right\} \right) +$$
$$+ i \, \mathrm{p.v.} \int_{-\infty}^{+\infty} \mathrm{d}k \, \left(\frac{\hat{F}_{\beta\alpha}(-\omega + k)}{-k} S_\beta(\omega) S^\dagger_\alpha(\omega) \rho + \frac{\hat{F}_{\beta\alpha}(-\omega + k)}{k} \rho S_\beta(\omega) S^\dagger_\alpha(\omega) \right). \quad \text{(A.38)}$$

The first term has clearly the structure of a Kossakowski-Lindblad dissipator, while the second one can be read as the action of a Hamiltonian generator $\mathbf{L}^{(1)}[\cdot] = -i[H^{(1)}, \cdot]$, once we define

$$H^{(1)} = \mathrm{p.v.} \int_{-\infty}^{+\infty} \mathrm{d}k \, \frac{\hat{F}_{\beta\alpha}(-\omega + k)}{k} S_\beta(\omega) S^\dagger_\alpha(\omega). \quad \text{(A.39)}$$

The spurious Hamiltonian $H^{(1)}$ is sometimes called *Lamb-shift* correction, and it is self-adjoint, as it should be, and this can be easily shown observing that $\hat{F}_{\beta\alpha}(x)^* = \hat{F}_{\alpha\beta}(x)$.

A.3. Positivity of the Kossakowski-Lindblad matrix

In this section we prove that the Kossakowski matrix appearing in the expression (A.38) of the operator $\mathbf{K}_3$ is positive, hence that the reduced dynamics generated by $\mathbf{K}_3$ is completely positive. We will make the assumption that the environment state ρ_E be a Gibbs state $\rho_E = e^{-\beta H_E}/\mathrm{Tr}(e^{-\beta H_E})$; namely, that the environment is a thermal reservoir, which is the case of the open quantum systems in which we are interested.

The positivity of the matrix of elements $\hat{F}_{\beta\alpha}(-\omega)$ corresponds to the condition

$$\sum_{\alpha,\beta=1}^{n} u_\alpha^* \hat{F}_{\beta\alpha}(-\omega) u_\beta \geq 0, \tag{A.40}$$

for every $|u\rangle = (u_1, \ldots, u_n) \in \mathbb{C}^n$.

Rewriting the $\hat{F}_{\beta\alpha}(-\omega)$ as Fourier transforms of the bath correlators, as in (A.31), we have

$$\begin{aligned}
\sum_{\alpha,\beta=1}^{n} u_\alpha^* \hat{F}_{\beta\alpha}(-\omega) u_\beta &= \int_{-\infty}^{+\infty} \mathrm{d}t\, e^{it\omega} \sum_{\alpha,\beta=1}^{n} u_\alpha^* F_{\alpha\beta}(t) u_\beta = \\
&= \int_{-\infty}^{+\infty} \mathrm{d}t\, e^{it\omega} \sum_{\alpha,\beta=1}^{n} u_\alpha^* u_\beta \mathrm{Tr}_{\mathrm{E}}(e^{itH_E} R_\alpha e^{-itH_E} R_\beta \rho_E) = \\
&= \sum_{\epsilon,\epsilon'} \int_{-\infty}^{+\infty} \mathrm{d}t\, e^{it\omega} u_\alpha^* u_\beta e^{it(\epsilon-\epsilon')} \langle \epsilon \,|\, R_\alpha \,|\, \epsilon' \rangle \langle \epsilon' \,|\, R_\beta \,|\, \epsilon \rangle\, r(\epsilon) = \\
&= \sum_{\epsilon,\epsilon'} r(\epsilon) \int_{-\infty}^{+\infty} \mathrm{d}t\, e^{it\omega} \langle \epsilon | \sum_{\alpha=1}^{n} u_\alpha^* R_\alpha | \epsilon' \rangle \langle \epsilon' | \sum_{\beta=1}^{n} u_\beta R_\beta | \epsilon \rangle = \\
&= 2\pi \sum_{\epsilon.\epsilon'} r(\epsilon) \delta(\omega - \epsilon + \epsilon') |\langle \epsilon | \sum_{\alpha=1}^{n} u_\alpha^* R_\alpha | \epsilon' \rangle|^2 \geq 0.
\end{aligned} \tag{A.41}$$

Where we have taken the trace with respect to the o.n.b. of H_E, $\{|\epsilon\rangle\}$, inserted a completeness $\sum_{\epsilon'} |\epsilon'\rangle\langle\epsilon'|$, and used the fact that the thermal Gibbs state $\rho_E = e^{-\beta H_E}/Z_\beta$ has the same energy eigenvectors of H_E: $\rho_E\,|\epsilon\rangle = r(\epsilon)\,|\epsilon\rangle$, with $r(\epsilon) > 0$.

A.4. Current expression for the quantum pumping model

The current $I(t)$ flowing in the circuit must be proportional to the probability density flux from one node to another, for example from a to b. If $|\psi_t(b)|^2$ is the probability of finding the free electron in the site b, then we have:

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}|\psi_t(b)|^2 &= \frac{\mathrm{d}}{\mathrm{d}t}|\langle b \,|\, \psi_t\rangle|^2 = \\
&= \langle b \,|\, -iH_S \,|\, \psi_t\rangle \langle \psi_t \,|\, b\rangle + \langle b \,|\, \psi_t\rangle \langle \psi_t \,|\, iH_S \,|\, b\rangle = \\
&= -i(-\gamma_0)\left(\left(\langle a \,|\, \psi_t\rangle + \langle c \,|\, \psi_t\rangle\right)\langle \psi_t \,|\, b\rangle\right) + i(-\gamma_0)\left(\langle b \,|\, \psi_t\rangle \left(\langle \psi_t \,|\, a\rangle + \langle \psi_t \,|\, c\rangle\right)\right) = \\
&= i\gamma_0(\langle \psi_t \,|\, b\rangle \langle a \,|\, \psi_t\rangle - \langle \psi_t \,|\, a\rangle \langle b \,|\, \psi_t\rangle + \langle \psi_t \,|\, b\rangle \langle c \,|\, \psi_t\rangle - \langle \psi_t \,|\, c\rangle \langle b \,|\, \psi_t\rangle) = \\
&= \langle i\gamma_0(|b\rangle \langle a| - |a\rangle \langle b|)\rangle_{\psi_t} + \langle i\gamma_0(|b\rangle \langle c| - |c\rangle \langle b|)\rangle_{\psi_t} \,,
\end{aligned} \tag{A.42}$$

where in the last passage we have written the result as sum of the expectation values of the two observables $i\gamma_0(|b\rangle \langle a| - |a\rangle \langle b|)$ and $i\gamma_0(|b\rangle \langle c| - |c\rangle \langle b|)$ on the state $|\psi_t\rangle$.

Thus the flux of probability from a to b is

$$\langle i\gamma_0(|b\rangle \langle a| - |a\rangle \langle b|)\rangle_{\psi_t} \,, \tag{A.43}$$

while the flux from b to c is

$$\langle i\gamma_0(|c\rangle \langle b| - |b\rangle \langle c|)\rangle_{\psi_t} \,. \tag{A.44}$$

Coherently, the variation in time of the probability density $|\psi_t(b)|^2$ is given by the difference between the flux from a to b and the flux from b to c.

The current from a to b is then determined by

$$I_{ab} = \gamma_0 \langle -ie(|b\rangle \langle a| - |a\rangle \langle b|)\rangle_{\psi_t} \tag{A.45}$$

where e is the elementary charge.

Writing this expression in the basis $\{|0\rangle, |x\rangle, |y\rangle\}$ by means of the transformation

$$\begin{aligned}
|a\rangle &= \frac{|0\rangle + \sqrt{2}\,|y\rangle}{\sqrt{3}} \\
|b\rangle &= \frac{\sqrt{2}\,|0\rangle + \sqrt{3}\,|x\rangle - |y\rangle}{\sqrt{6}} \\
|c\rangle &= \frac{\sqrt{2}\,|0\rangle - \sqrt{3}\,|x\rangle - |y\rangle}{\sqrt{6}} \,,
\end{aligned}$$

one has

$$\begin{aligned}
I_{ab} = \frac{ie\gamma_0}{3\sqrt{2}}\Big(&\sqrt{3}\,|0\rangle \langle x| - |0\rangle \langle y| + 2\,|y\rangle \langle 0| + \sqrt{6}\,|y\rangle \langle x| - \\
&-2\,|0\rangle \langle y| - 3\,|x\rangle \langle 0| - \sqrt{6}\,|x\rangle \langle y| + |y\rangle \langle 0|\Big)
\end{aligned}$$

This expression gives I_{ab} in the most general case, when all the states $|0\rangle, |x\rangle$ and $|y\rangle$ are taken into account; in the pseudospin-1/2 approximation however the transitions involving $|0\rangle$ are neglected, therefore all the terms involving this state can be dropped from the above formula, whence

$$I_{ab} = \frac{ie\gamma_0}{\sqrt{3}}\Big(|y\rangle\langle x| - |x\rangle\langle y| \Big) = \frac{e\gamma_0}{\sqrt{3}}\sigma^y$$

where the last passage follows from choosing

$$|x\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad |y\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} . \tag{A.46}$$

Finally, the expectation value of I_{ab} is

$$I(t) = \langle I_{ab}\rangle_{\rho_S(t)} = I_0\langle\sigma^y\rangle_{\rho_S(t)} = I_0\mathrm{Tr}(\rho_S(t)\sigma^y)\,, \tag{A.47}$$

where $I_0 = e\gamma_0/\sqrt{3}$ and $\rho_S(t)$ is the 2×2 density matrix describing the system.

A.5. Master Equation for the quantum pumping model

We summarize the derivation of the Master Equation for the open quantum system analyzed in Chapter 4, following the general procedure based on projectors, used in Appendix A.1.

We introduce the projector $\mathbf{P}$ on $\mathcal{S}(S+E)$:

$$\mathbf{P}[\rho_{S+E}] \equiv \mathrm{Tr_E}(\rho_{S+E}) \otimes \rho_E \tag{A.48}$$

and its orthogonal operator $\mathbf{Q} \equiv \mathbf{1} - \mathbf{P}$.

$\mathbf{P}$ maps any factorized state into itself, while $\mathbf{Q}$ annihilates them:

$$\mathbf{P}[\rho_S \otimes \rho_E] = \rho_S \otimes \rho_E \tag{A.49}$$
$$\mathbf{Q}[\rho_S \otimes \rho_E] = 0 \tag{A.50}$$

Splitting the Liouville-Von Neumann equation (4.34) into two parts we get:

$$\partial_t\mathbf{P}\tilde{\rho} = \tilde{L}^{PP}_{S+E}(t)[\mathbf{P}\tilde{\rho}] + \tilde{L}^{PQ}_{S+E}(t)[\mathbf{Q}\tilde{\rho}] \tag{A.51}$$
$$\partial_t\mathbf{Q}\tilde{\rho} = \tilde{L}^{QP}_{S+E}(t)[\mathbf{P}\tilde{\rho}] + \tilde{L}^{QQ}_{S+E}(t)[\mathbf{Q}\tilde{\rho}] \tag{A.52}$$

where

$$
\begin{aligned}
\tilde{L}_{S+E}^{PP} &= \mathbf{P} \circ \tilde{L}_{S+E} \circ \mathbf{P} \\
\tilde{L}_{S+E}^{PQ} &= \mathbf{P} \circ \tilde{L}_{S+E} \circ \mathbf{Q} \\
\tilde{L}_{S+E}^{QP} &= \mathbf{Q} \circ \tilde{L}_{S+E} \circ \mathbf{P} \\
\tilde{L}_{S+E}^{QQ} &= \mathbf{Q} \circ \tilde{L}_{S+E} \circ \mathbf{Q}
\end{aligned}
$$

In the following, in order to improve the readability, we will often write ρ instead of $\tilde{\rho}_{S+E}$, $L^{PP}(t)$ for $\tilde{L}_{S+B}^{PP}(t)$ and so on, and we will omit the variable t where possible.

The formal solution for (A.52) is:

$$
\mathbf{Q}\rho = U_{QQ}(t)[\rho_0] + \int_0^t \mathrm{d}u\, U_{QQ}(t,u) L^{QP}(u) \mathbf{P}\rho(u) \tag{A.53}
$$

where U_{QQ} is the solution of

$$
\frac{\mathrm{d}}{\mathrm{d}t} U_{QQ}(t, t_0) = L^{QQ}(t) U_{QQ}(t, t_0) \tag{A.54}
$$

We look for ρ starting from a factorized initial state $\rho_0 = \rho_S(0) \otimes \rho_E$.

Inserting (A.53) in (A.51):

$$
\partial_t \mathbf{P}\rho = L^{PP}(t)\mathbf{P}\rho + L^{PQ}(t) \int_0^t \mathrm{d}u\, U_{QQ}(t,u) L^{QP}(u) \mathbf{P}\rho(u)
$$

The first term is:

$$
\begin{aligned}
L^{PP}\mathbf{P}[\rho] &= \\
&= \mathbf{P}\left(-i[H_{\text{eff}} \otimes \mathbf{1}_E + \mathbf{1}_S \otimes H_E + \tilde{H}_{SE}\,,\, \mathrm{Tr_E}(\rho) \otimes \rho_E]\right) = \\
&= \mathbf{P}\left(-i[H_{\text{eff}}\,, \mathrm{Tr_E}(\rho)] \otimes \rho_E\right) = \\
&= -i[H_{\text{eff}}\,,\, \mathrm{Tr_E}(\rho)] \otimes \rho_E
\end{aligned} \tag{A.55}
$$

This follows from

$$
[H_E, \rho_E] = 0 \tag{A.56}
$$

$$
\mathrm{Tr_E}(H_E \rho_E) = 0 \tag{A.57}
$$

$$
\mathrm{Tr_E}(q_{\xi,\nu} \rho_E) = 0 \tag{A.58}
$$

In order to calculate the second term we expand $L^{PQ}[X]$ on a generic matrix $X \in M_n(\mathbb{C}) \otimes M_m(\mathbb{C})$:

$$\begin{aligned} L^{PQ}[X] &= \mathbf{P} \circ L[X] - \mathbf{P} \circ L \circ \mathbf{P}[X] = \\ &= (\mathrm{Tr_E}(L[X]) - \mathrm{Tr_E}(L[\mathrm{Tr_E}(X) \otimes \rho_E])) \otimes \rho_E = \\ &= -i \,\mathrm{Tr_E}\left(\Big[H_{\text{eff}} \otimes \mathbf{1}_E + \mathbf{1}_S \otimes \tilde{H}_E + \tilde{H}_{SE}\,,\, X\Big]\right) \otimes \rho_E + \\ &\quad + i[H_{\text{eff}}\,,\, \mathrm{Tr_E}(X)] \otimes \rho_E \end{aligned} \tag{A.59}$$

The first and fourth term cancel out while the second vanishes and we have:

$$L^{PQ}[X] = -i\,\mathrm{Tr_E}([\tilde{H}_{SE}, X]) \otimes \rho_E$$

So the Master Equation takes the form:

$$\partial_t \mathbf{P}\rho = -i[H_{\text{eff}}\,,\, \mathrm{Tr_E}(\rho)] \otimes \rho_E - i\,\mathrm{Tr_E}\left[\tilde{H}_{SE}(t)\,,\, \int_0^t \mathrm{d}u\, U_{QQ}(t,u) L^{QP}(u)\mathbf{P}\rho\right] \otimes \rho_E$$

Following a very similar reasoning we have:

$$L^{QP}[\rho] = -i[\tilde{H}_{SE}\,,\, \mathrm{Tr_E}(\rho) \otimes \rho_E]$$

And finally we get the Master Equation

$$\begin{aligned} \partial_t \mathbf{P}\rho &= \partial_t \mathrm{Tr_E}(\rho) \otimes \rho_E = \\ &= -i[H_{\text{eff}}\,,\, \mathrm{Tr_E}(\rho)] \otimes \rho_E + \\ &\quad - \int_0^t \mathrm{d}u\, \mathrm{Tr_E}\Big[\tilde{H}_{SE}(t)\,,\, U_{QQ}(t,u)[\tilde{H}_{SE}(u), \rho(u)]\Big] \otimes \rho_E \end{aligned}$$

which can be written with respect to the reduced dynamics ($\tilde{\rho}_S = \mathrm{Tr_E}(\rho)$):

$$\partial_t \tilde{\rho}_S \;=\; -i[H_{\text{eff}}\,,\, \tilde{\rho}_S] - \int_0^t \mathrm{d}u\, \mathrm{Tr_E}\Big[\tilde{H}_{SE}(t)\,,\, U_{QQ}(t,u)[\tilde{H}_{SE}(u), \tilde{\rho}_S(u) \otimes \rho_E]\Big] \tag{A.60}$$

The integral version of this Master Equation is

$$\begin{aligned} \tilde{\rho}_S(t) &= e^{t\tilde{L}_S}\tilde{\rho}_S(0) + \\ &\quad - \int_0^t \mathrm{d}u\, e^{(t-u)\tilde{L}_S}\Big[\int_0^u \mathrm{d}v\, \mathrm{Tr_E}\Big[\tilde{H}_{SE}(u)\,,\, U_{QQ}(u,v)[\tilde{H}_{SE}(v), \tilde{\rho}_S(u) \otimes \rho_E]\Big]\Big] \end{aligned} \tag{A.61}$$

We operate a change of coordinates in the double integral $\int_0^t \mathrm{d}u \int_0^u \mathrm{d}v$:

$$\begin{cases} x(u,v) \equiv v \\ y(u,v) \equiv -u \end{cases} \Rightarrow \begin{cases} u = -y \\ v = x \end{cases}$$

$$det \frac{\partial(x,y)}{\partial(u,v)} = \begin{vmatrix} 0 & 1 \\ -1 & 0 \end{vmatrix} = 1$$

Thus $\int_0^t \mathrm{d}u \int_0^u \mathrm{d}v f(u,v) = \int_0^t \mathrm{d}x \int_{-t}^{-x} \mathrm{d}y f(-y,x)$, and then, with another change of variable:

$$w \equiv -x - y$$

$$\Rightarrow \int_{-t}^{-x} \mathrm{d}y = -\int_{-x-(-t)}^{-x-(-x)} \mathrm{d}w = \int_0^{t-x} \mathrm{d}w$$

and the integral in (A.61) can be rewritten as

$$\int_0^t \mathrm{d}x\, e^{(t-x)\tilde{L}_S} \int_0^{t-x} \mathrm{d}w\, e^{-w\tilde{L}_S} \mathrm{Tr_E}\Big[\tilde{H}_{SE}(w+x)\,, U_{QQ}(w+x,x)[\tilde{H}_{SE}(x), \tilde{\rho}_S(x) \otimes \rho_E]\Big] \tag{A.62}$$

Now we want to study this integral in the *weak coupling limit* condition: we assume that the ratio τ_E/τ_S of the typical decay time-scales of the correlations between the system and the environment is very small. For the sake of simplicity we replace the coupling constants $\lambda_{\xi\nu}$ with one single parameter λ, appearing in $\tilde{H}_{SE}$.

Thus the dissipation effects are relevant only on the very slow time-scale $\tau = \lambda^2 t$. Setting $t = \tau/\lambda^2$ in the dw integration in (A.62):

$$\lambda^2 \sum_{\xi,\nu,\chi,\mu} \int_0^{\frac{\tau}{\lambda^2}-x} \mathrm{d}w\, e^{-w\tilde{L}_S} \cdot$$
$$\cdot \mathrm{Tr_E}\big[\tilde{\sigma}^\xi(w+x) \otimes q_{\xi,\nu}\,,\, U_{QQ}(w+x,x)[\tilde{\sigma}^\chi(x) \otimes q_{\chi,\mu}, \tilde{\rho}_S(x) \otimes \rho_E]\big] \tag{A.63}$$

We search for an approximated expression for U_{QQ}, solution of the equation

$$\frac{\mathrm{d}}{\mathrm{d}t} U_{QQ}(t,s) = \tilde{L}^{QQ}_{S+E}(t) U_{QQ}(t,s) \tag{A.64}$$

Introducing the time-ordered operator $\mathcal{T}$ we can write

$$U_{QQ}(w+x,x)=\mathcal{T}\left(\exp\int_x^{w+x}\mathrm{d}u\,\tilde{L}^{QQ}_{S+E}(u)\right)=$$
$$=\mathcal{T}\left(\exp\left\{w(\tilde{L}_S+\tilde{L}_E)^{QQ}-i\lambda\sum_{\xi,\nu}\int_x^{w+x}\mathrm{d}u\,\mathbf{Q}\circ[\tilde{\sigma}^{\xi}(u)\otimes q_{\xi,\nu}\,,\,\cdot]\circ\mathbf{Q}\right\}\right) \quad (A.65)$$

In the limit $\lambda\to 0$ this becomes

$$U_{QQ}(w+x,x)\simeq\exp\left(w(\tilde{L}_S+\tilde{L}_E)^{QQ}\right) \quad (A.66)$$

while in the integral (A.63) a correction of the λ^2 order survives:

$$\lambda^2\sum_{\xi,\nu,\chi,\mu}\int_0^{+\infty}\mathrm{d}w\,e^{-w\tilde{L}_S}\cdot$$
$$\cdot\,\mathrm{Tr_E}\Big[\tilde{\sigma}^{\xi}(w+x)\otimes q_{\xi,\nu}\,,\,e^{w(\tilde{L}_S+\tilde{L}_E)^{QQ}}[\tilde{\sigma}^{\chi}(x)\otimes q_{\chi,\mu},\tilde{\rho}_S(x)\otimes\rho_E]\Big] \quad (A.67)$$

In the end the double integral (A.62) becomes:

$$-\int_0^t\mathrm{d}x\,e^{(t-x)\tilde{L}_S}\sum_{\xi,\nu,\chi,\mu}2m\sqrt{\omega_\nu\omega_\mu}\lambda_{\xi,\nu}\lambda_{\chi,\mu}\int_0^{+\infty}\mathrm{d}w\,e^{-w\tilde{L}_S}\cdot$$
$$\cdot\,\mathrm{Tr_E}\Big[\tilde{\sigma}^{\xi}(w+x)\otimes q_{\xi,\nu}\,,\,e^{w(\tilde{L}_S+\tilde{L}_E)^{QQ}}[\tilde{\sigma}^{\chi}(x)\otimes q_{\chi,\mu},\tilde{\rho}_S(x)\otimes\rho_E]\Big] \quad (A.68)$$

It is important to recall that we are interested in the *dissipator* $\mathbf{D}$ appearing in the Master Equation (2.31), which is a differential equation. One can notice that the above formula, and the way in which it has been derivated, corresponds exactly to the action of the operator $\mathbf{K}_2$ seen in (2.61). In the rest of this section we will derive an explicit expression for $\mathbf{K}_2$.

We define the self-adjoint operators on $\mathcal{H}_S$:

$$\Lambda_{\xi\nu}(x)\equiv\sqrt{2m\omega_\nu}\lambda_{\xi,\nu}\tilde{\sigma}^{\xi}(x) \quad (A.69)$$

The second argument of the external commutator in (A.68) can be written

$$e^{w(\tilde{L}_S+\tilde{L}_E)^{QQ}}\sum_{\chi,\mu}\left(\Lambda_{\chi\mu}(x)\tilde{\rho}_S(x)\otimes q_{\chi,\mu}\rho_E-\tilde{\rho}_S(x)\Lambda_{\chi\mu}(x)\otimes\rho_E q_{\chi,\mu}\right) \quad (A.70)$$

where of course we can factorize $e^{w(\tilde{L}_S+\tilde{L}_E)^{QQ}}=e^{w\tilde{L}_S^{QQ}}\otimes e^{w\tilde{L}_E^{QQ}}$

We show that $\tilde{L}_S\mathbf{Q}=\mathbf{Q}\tilde{L}_S$.

For every $\rho \in \mathcal{S}(S+E)$:

$$
\begin{aligned}
[\tilde{L}_S, \mathbf{Q}]\rho = \tilde{L}_S[(\mathbf{1}-\mathbf{P})\rho] - (1-\mathbf{P})[\tilde{L}_S\rho] = \\
= \tilde{L}_S\rho + i[H_{\text{eff}}, \mathrm{Tr}_{\mathrm{E}}\rho] \otimes \rho_E - \tilde{L}_S\rho + \mathrm{Tr}_{\mathrm{E}}(\tilde{L}_S\rho) \otimes \rho_E = \\
= i[H_{\text{eff}}, \mathrm{Tr}_{\mathrm{E}}\rho] \otimes \rho_E - i\mathrm{Tr}_{\mathrm{E}}[H_{\text{eff}} \otimes \mathbf{1}_E, \rho] \otimes \rho_E = 0
\end{aligned}
\tag{A.71}
$$

(the last equality is proved in the same way as (A.8)).

Also $\tilde{L}_E\mathbf{Q} = \mathbf{Q}\tilde{L}_E$:

$$
\begin{aligned}
&[\tilde{L}_E, \mathbf{Q}]\rho = \\
&= -i[\mathbf{1}_S \otimes H_E, \rho - \mathrm{Tr}_{\mathrm{E}}(\rho) \otimes \rho_E] - (-i[\mathbf{1}_S \otimes H_E, \rho] + i\mathrm{Tr}_{\mathrm{E}}[\mathbf{1}_S \otimes H_E, \rho] \otimes \rho_E) = \\
&= i[\mathbf{1}_S \otimes H_E, \mathrm{Tr}_{\mathrm{E}}(\rho) \otimes \rho_E] - i\mathrm{Tr}_{\mathrm{E}}[\mathbf{1}_S \otimes H_E, \rho] \otimes \rho_E = 0
\end{aligned}
\tag{A.72}
$$

since $[H_E, \rho_E] = 0$ and $\mathrm{Tr}_{\mathrm{E}}[\mathbf{1}_S \otimes H_E, \rho] = 0$ (cfr. (A.9)).

This means that we can factorize $e^{w(\tilde{L}_S+\tilde{L}_E)^{QQ}}$ in (A.70), drop the ^{QQ} indices and write

$$
e^{w\tilde{L}_E}[q_{\chi,\mu}\rho_E] = e^{-iwH_E} q_{\chi,\mu} e^{iwH_E} \rho_E =: q_{\chi,\mu}(w)\rho_E \tag{A.73}
$$

ρ_E being the equilibrium state.

The trace in (A.68) can be rewritten

$$
\begin{aligned}
\sum_{\xi,\nu}\sum_{\chi,\mu} \mathrm{Tr}_{\mathrm{E}} \Big(\Big[\Lambda_{\xi\nu}(w+x) \otimes q_{\xi,\nu}\ ,\ e^{w\tilde{L}_S}[\Lambda_{\chi,\mu}(x)\tilde{\rho}_S(x)] \otimes q_{\chi,\mu}(w)\rho_E + \\
- e^{w\tilde{L}_S}[\tilde{\rho}_S(x)\Lambda_{\chi,\mu}(x)] \otimes \rho_E q_{\chi,\mu}(w) \Big] \Big)
\end{aligned}
\tag{A.74}
$$

For each choice of indices we have four terms to trace over the environment, but for the ciclity property they actually reduce to two:

$$
\mathrm{Tr}_{\mathrm{E}}(q_{\xi,\nu} q_{\chi,\mu}(w)\rho_E) \tag{A.75a}
$$

$$
\mathrm{Tr}_{\mathrm{E}}(q_{\xi,\nu}\rho_E q_{\chi,\mu}(w)) \tag{A.75b}
$$

In second quantization $q_{\chi,\mu}(w) = \frac{1}{\sqrt{2m\omega_\mu}}\left(a^\dagger_{\chi\mu}(w) + a_{\chi\mu}(w)\right)$, and the differential equation for $a^\dagger_{\chi\mu}(w)$

$$
\frac{\mathrm{d}}{\mathrm{d}w} a^\dagger_{\chi\mu}(w) = -ie^{-iwH_E}[H_E, a^\dagger_{\chi\mu}]e^{iwH_E} = -i\omega_\mu e^{-iwH_E} a^\dagger_{\chi\mu} e^{iwH_E},
$$

has the solution

$$
a^\dagger_{\chi\mu}(w) = e^{-iw\omega_\mu} a^\dagger_{\chi\mu}(w).
$$

The thermal equilibrium state of the environment has the usual form:

$$\rho_E = \frac{e^{-\beta H_E}}{Z_\beta}$$

$$Z_\beta = \prod_{\nu=0}^{N} \sum_{n_{\nu z}, n_{\nu x}=0}^{\infty} e^{-\beta\omega_\nu(n_{\nu z}+n_{\nu x}+1)}$$

and Z_β is the partition function, whose expression is easily derived if we rewrite H_E in second quantization

$$H_E = \sum_{\nu=0}^{N} \sum_{\xi=z,x} \omega_\nu \left(a^\dagger_{\xi\nu} a_{\xi\nu} + \frac{1}{2} \right)$$

$$e^{-\beta H_E} = \bigotimes_{\nu=0}^{N} e^{-\beta\omega_\nu \sum_\xi \left(a^\dagger_{\xi\nu} a_{\xi\nu} + \frac{1}{2}\right)} \tag{A.76}$$

Consequently the first trace (A.75a)

$$\mathrm{Tr_E}(q_{\xi,\mu} q_{\chi,\mu}(w)\rho_E) = \mathrm{Tr_E}\left(q_{\xi,\nu} \frac{1}{\sqrt{2m\omega_\mu}} \left(e^{-iw\omega_\mu} a^\dagger_{\chi\mu} + e^{iw\omega_\mu} a_{\chi\mu}\right) \frac{e^{-\beta H_E}}{Z_\beta} \right) \tag{A.77}$$

can be calculated with respect to the Fock orthonormal basis formed by all the possible tensor products in $\bigotimes_{\nu=0}^{N} \mathcal{H}_{E,\nu}$ of the eigenstates $\{|n_{\nu x}, n_{\nu z}\rangle\}_{n_{\nu x}.n_{\nu z}}$ of the set of Hamiltonians of each oscillator $H_{E,\nu} = \sum_{\xi=z,x} \omega_\nu \left(a^\dagger_{\xi\nu} a_{\xi\nu} + \frac{1}{2} \right)$:

$$a^\dagger_{\xi\nu} a_{\xi\nu} |n_{\nu x}, n_{\nu z}\rangle = (n_{\nu x}\delta_{\xi x} + n_{\nu z}\delta_{\xi z}) |n_{\nu x}, n_{\nu z}\rangle \tag{A.78}$$

$$H_{E,\nu} |n_{\nu x}, n_{\nu z}\rangle = \omega_\nu (n_{\nu x} + n_{\nu z} + \frac{1}{2}) |n_{\nu x}, n_{\nu z}\rangle \tag{A.79}$$

Due to the orthogonality, only the following terms survive in (A.77):

$$\frac{1}{Z_\beta \sqrt{2m\omega_\mu}} \mathrm{Tr_E}\left(\frac{e^{-iw\omega_\mu} a_{\chi\mu} a^\dagger_{\chi\mu} e^{-\beta H_E}}{\sqrt{2m\omega_\mu}} + \frac{e^{iw\omega_\mu} a^\dagger_{\chi\mu} a_{\chi\mu} e^{-\beta H_E}}{\sqrt{2m\omega_\mu}} \right) \tag{A.80}$$

With respect to the Fock basis (A.78), the trace of a generic operator A can be written

$$\mathrm{Tr_E} A = \sum_{n_{0x}, n_{0z}=0}^{\infty} \dots \sum_{n_{Nx}, n_{Nz}=0}^{\infty} \langle n_{0x}, n_{0z}| \dots \langle n_{Nx}, n_{Nz} \,|\, A \,|\, n_{0x}, n_{0z}\rangle \dots |n_{Nx}, n_{Nz}\rangle \tag{A.81}$$

and we have

$$\mathrm{Tr}_{\mathrm{E}}(a_{\chi\mu}a^{\dagger}_{\chi\mu}e^{-\beta H_E}) = \sum_{n_{0x},n_{0z}=0}^{\infty} \cdots \sum_{n_{Nx},n_{Nz}=0}^{\infty} \prod_{\nu=0}^{N} e^{-\beta(n_{\nu x}+n_{\nu z}+1)\omega_\nu}(n_{\mu\chi}+1) =$$

$$= \prod_{\nu\neq\mu} \sum_{n_{\nu x},n_{\nu z}=0}^{\infty} e^{-\beta(n_{\nu x}+n_{\nu z}+1)\omega_\nu} \sum_{n_{\mu x},n_{\mu z}=0}^{\infty} e^{-\beta(n_{\mu x}+n_{\mu z}+1)\omega_\mu}(n_{\mu\chi}+1) \quad \text{(A.82)}$$

Now we use the geometric series and its derivative to evaluate the second sum (here n stands for either $n_{\mu x}$ or $n_{\mu z}$, depending on the value of χ)

$$\sum_n \left(ne^{-\beta\omega_\mu n} + e^{-\beta\omega_\mu n}\right) = \frac{1}{1-e^{-\beta\omega_\mu}} + \frac{1}{-\beta}\frac{\mathrm{d}}{\mathrm{d}\omega_\mu}\frac{1}{1-e^{-\beta\omega_\mu}} =$$

$$= \frac{e^{\beta\omega_\mu/2}}{e^{\beta\omega_\mu/2}-e^{-\beta\omega_\mu/2}} + \frac{e^{-\beta\omega_\mu}}{(1-e^{-\beta\omega_\mu})^2} =$$

$$= \frac{e^{\beta\omega_\mu/2}}{e^{\beta\omega_\mu/2}-e^{-\beta\omega_\mu/2}} + \frac{e^{-\beta\omega_\mu}}{e^{-\beta\omega_\mu}\left(e^{\beta\omega_\mu/2}-e^{-\beta\omega_\mu/2}\right)^2} =$$

$$= \frac{e^{\beta\omega_\mu}}{\left(e^{\beta\omega_\mu/2}-e^{-\beta\omega_\mu/2}\right)^2} \quad \text{(A.83)}$$

that must be multiplied by

$$e^{-\beta\omega_\mu}\sum_{n=0}^{\infty} e^{-\beta\omega_\mu n} \quad \text{(A.84)}$$

so the second sum becomes:

$$\frac{1}{1-e^{-\beta\omega_\mu}}\frac{1}{\left(e^{\beta\omega_\mu/2}-e^{-\beta\omega_\mu/2}\right)^2} \quad \text{(A.85)}$$

In order to evaluate the first factor in (A.82), we observe that the partition function for the ν-th oscillator is

$$Z_\nu(\beta) = \sum_{n_{\nu z},n_{\nu x}=0}^{\infty} e^{-\beta\omega_\nu(n_{\nu z}+n_{\nu x}+1)} = \frac{1}{\left(e^{\beta\omega_\nu/2}-e^{-\beta\omega_\nu/2}\right)^2} \quad \text{(A.86)}$$

while the total partition function is

$$Z_\beta = \prod_\nu Z_\nu(\beta) \quad \text{(A.87)}$$

Consequently we can write the first factor as

$$\prod_{\nu\neq\mu}\sum_{n_{\nu x},n_{\nu z}=0}^{\infty} e^{-\beta(n_{\nu x}+n_{\nu z}+1)\omega_\nu} = \frac{Z_\beta}{Z_\mu(\beta)} \tag{A.88}$$

and the final expression for (A.82) becomes

$$\mathrm{Tr_E}(a_{\chi\mu}a^\dagger_{\chi\mu}e^{-\beta H_E}) = \frac{Z_\beta}{Z_\mu(\beta)}\frac{1}{1-e^{-\beta\omega_\mu}}\frac{1}{(e^{\beta\omega_\mu/2}-e^{-\beta\omega_\mu/2})^2} \tag{A.89}$$

In a very similar way we get the final expression for the second term in (A.80):

$$\mathrm{Tr_E}(a^\dagger_{\chi\mu}a_{\chi\mu}e^{-\beta H_E}) = \frac{Z_\beta}{Z_\mu(\beta)}\frac{e^{-\beta\omega_\mu}}{1-e^{-\beta\omega_\mu}}\frac{1}{(e^{\beta\omega_\mu/2}-e^{-\beta\omega_\mu/2})^2} \tag{A.90}$$

Going back to (A.77)

$$\begin{aligned}
\mathrm{Tr_E}(q_{\xi,\mu}q_{\chi,\mu}(w)\rho_E) &= \mathrm{Tr_E}\left(q_{\xi,\nu}\frac{1}{\sqrt{2m\omega_\mu}}\left(e^{-iw\omega_\mu}a^\dagger_{\chi\mu}+e^{iw\omega_\mu}a_{\chi\mu}\right)\frac{e^{-\beta H_E}}{Z_\beta}\right) = \\
&= \frac{1}{2m\omega_\mu Z_\mu(\beta)}\frac{e^{-\beta\omega_\mu}}{1-e^{-\beta\omega_\mu}}\left(\frac{e^{i\omega_\mu w}}{(e^{\beta\omega_\mu/2}-e^{-\beta\omega_\mu/2})^2}+\frac{e^{\beta\omega_\mu}e^{-i\omega_\mu w}}{(e^{\beta\omega_\mu/2}-e^{-\beta\omega_\mu/2})^2}\right) = \\
&= \frac{1}{2m\omega_\mu Z_\mu(\beta)}\frac{e^{-\beta\omega_\mu/2}}{1-e^{-\beta\omega_\mu}}\left(\frac{\cos\omega_\mu w(e^{\beta\omega_\mu/2}+e^{-\beta\omega_\mu/2})-i\sin\omega_\mu w(e^{\beta\omega_\mu/2}-e^{-\beta\omega_\mu/2})}{(e^{\beta\omega_\mu/2}-e^{-\beta\omega_\mu/2})^2}\right) = \\
&= \frac{1}{2m\omega_\mu Z_\mu(\beta)}\frac{1}{(e^{\beta\omega_\mu/2}-e^{-\beta\omega_\mu/2})^2}\left(\cos\omega_\mu w\coth\frac{\beta\omega_\mu}{2}-i\sin\omega_\mu w\right)
\end{aligned} \tag{A.91}$$

and using (A.86)

$$\mathrm{Tr_E}(q_{\xi,\mu}q_{\chi,\mu}(w)\rho_E) = \frac{\cos\omega_\mu w\coth\frac{\beta\omega_\mu}{2}-i\sin\omega_\mu w}{2m\omega_\mu} \tag{A.92}$$

It is straightforward to observe that the other trace (A.75b) is exactly the complex conjugate of the latter:

$$\mathrm{Tr_E}(q_{\xi,\nu}\rho_E q_{\chi,\mu}(w)) = \frac{\cos\omega_\mu w\coth\frac{\beta\omega_\mu}{2}+i\sin\omega_\mu w}{2m\omega_\mu} \tag{A.93}$$

We can go back to the trace (A.74) and perform the sum over $\chi = x, z$ and $\mu = 0, \ldots, N$ (since $\xi = \chi$ and $\nu = \mu$ as seen above).

$$\sum_{\chi,\mu}\Big(\Big[\Lambda_{\chi\mu}(w+x)\otimes q_{\chi,\mu}\,,\; e^{w\tilde{L}_S}[\Lambda_{\chi,\mu}(x)\tilde{\rho}_S(x)]\otimes q_{\chi,\mu}(w)\rho_E +$$
$$-e^{w\tilde{L}_S}[\tilde{\rho}_S(x)\Lambda_{\chi,\mu}(x)]\otimes\rho_E q_{\chi,\mu}(w)\Big]\Big) =$$
$$= \sum_{\chi,\mu}\lambda^2_{\chi,\mu}\left(\cos\omega_\mu w\coth\frac{\beta\omega_\mu}{2} - i\sin\omega_\mu w\right)\left[\tilde{\sigma}^\chi(w+x),\, e^{w\tilde{L}_S}[\tilde{\sigma}^\chi(x)\tilde{\rho}_S(x)]\right] +$$
$$+\sum_{\chi,\mu}\lambda^2_{\chi,\mu}\left(\cos\omega_\mu w\coth\frac{\beta\omega_\mu}{2} + i\sin\omega_\mu w\right)\left[e^{w\tilde{L}_S}[\tilde{\rho}_S(x)\tilde{\sigma}^\chi(x)],\, \tilde{\sigma}^\chi(w+x)]\right] \quad \text{(A.94)}$$

We can now introduce a continuous spectral density $J_\chi(k)$ defined by:

$$J_\chi(k) \equiv \sum_\mu \lambda^2_{\chi,\mu}\delta(k-\omega_\mu) \quad \text{(A.95)}$$

and substitute the sum over the μ-frequencies with an integral, and define

$$G_\chi(w) \equiv \int_0^{+\infty} \mathrm{d}k\, J_\chi(k)\left(\cos kw\coth\frac{\beta k}{2} - i\sin kw\right) \quad \text{(A.96)}$$

Finally we have to multiply on the left by $e^{-w\tilde{L}_S}$ and integrate over w in order to get the final expression for $\mathbf{K}_2$, from the integral version (A.68)

$$\mathbf{K}_2[\tilde{\rho}_S(t)] = -\sum_{\chi=z,x}\int_0^{+\infty}\mathrm{d}w\,\Big\{G_\chi(w)\left[e^{-w\tilde{L}_S}\tilde{\sigma}^\chi(w+t),\,\tilde{\sigma}^\chi(t)\tilde{\rho}_S(t)\right] +$$
$$+\,G^*_\chi(w)\left[\tilde{\rho}_S(t)\tilde{\sigma}^\chi(t),\,e^{-w\tilde{L}_S}\tilde{\sigma}^\chi(w+t)\right]\Big\}. \quad \text{(A.97)}$$

which gives the (4.38) Master Equation that we have presented in 4.2.

A.6. Time independence of the Master Equation

Here we show the time independence of eq. (4.50) and, in turn, of the Master Equation in the rotated frame.

$$\sum_{\xi=x,z} R(-\Omega t)_{\eta\xi}R(\Omega(w+t))_{\xi\chi} = \sum_{\substack{\xi=x,y,z\\ \Theta=x,y,z}} R(-\Omega t)_{\eta\Theta}P^{xz}_{\Theta\xi}R(\Omega(w+t))_{\xi\chi} =$$
$$\left(R(-\Omega t)P^{xz}R(\omega(w+t)\right)_{\eta\chi}, \quad \text{(A.98)}$$

where

$$P^{xz} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{A.99}$$

Since $R(-\Omega t)P^{xz} = P^{xz}R(-\Omega t)$, we have that (A.98) becomes

$$\begin{aligned} &\sum_{\xi=x,z} R(-\Omega t)_{\eta\xi} R(\Omega(w+t))_{\xi\chi} = \\ &\qquad (P^{xz}R(-\Omega t)R(\Omega(w+t))_{\eta\chi} = \\ &\qquad\qquad (P^{xz}R(\Omega w))_{\eta\chi} = \tilde{R}(\Omega w)_{\eta\chi}, \end{aligned} \tag{A.100}$$

having used the group properties of the rotation matrix R and defined

$$\tilde{R}(\Omega w) \equiv \begin{pmatrix} \cos\Omega w & 0 & \sin\Omega w \\ 0 & 0 & 0 \\ -\sin\Omega w & 0 & \cos\Omega w \end{pmatrix} \tag{A.101}$$

A.7. Master Equation in the Kossakowski-Lindblad form

In order to obtain the final form of the operator (4.52) we work out the matricial products in (4.50)

$$\begin{aligned} &\sum_{\eta=x,y,z} \Lambda^{-1}_{\tau\eta} \tilde{R}(\Omega w)_{\eta\chi} = \\ &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & \frac{\Delta}{\omega'} & \frac{\Omega}{\omega'} \\ 0 & -\frac{\Omega}{\omega'} & \frac{\Delta}{\omega'} \end{pmatrix} \begin{pmatrix} \cos\Omega w & 0 & \sin\Omega w \\ 0 & 0 & 0 \\ -\sin\Omega w & 0 & \cos\Omega w \end{pmatrix} = \begin{pmatrix} \cos\Omega w & 0 & \sin\Omega w \\ -\frac{\Omega}{\omega'}\sin\Omega w & 0 & \frac{\Omega}{\omega'}\cos\Omega w \\ -\frac{\Delta}{\omega'}\sin\Omega w & 0 & \frac{\Delta}{\omega'}\cos\Omega w \end{pmatrix} \equiv X \end{aligned} \tag{A.102}$$

$$\sum_{\chi=x,y,z} X_{\tau\chi}\Lambda_{\chi\mu} = \begin{pmatrix} \cos\Omega w & 0 & \sin\Omega w \\ -\frac{\Omega}{\omega'}\sin\Omega w & 0 & \frac{\Omega}{\omega'}\cos\Omega w \\ -\frac{\Delta}{\omega'}\sin\Omega w & 0 & \frac{\Delta}{\omega'}\cos\Omega w \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \frac{\Delta}{\omega'} & -\frac{\Omega}{\omega'} \\ 0 & \frac{\Omega}{\omega'} & \frac{\Delta}{\omega'} \end{pmatrix} =$$

$$= \begin{pmatrix} \cos\Omega w & \frac{\Omega}{\omega'}\sin\Omega w & \frac{\Delta}{\omega'}\sin\Omega w \\ -\frac{\Omega}{\omega'}\sin\Omega w & \frac{\Omega^2}{\omega'^2}\cos\Omega w & \frac{\Delta\Omega}{\omega'^2}\cos\Omega w \\ -\frac{\Delta}{\omega'}\sin\Omega w & \frac{\Delta\Omega}{\omega'^2}\cos\Omega w & \frac{\Delta^2}{\omega'^2}\cos\Omega w \end{pmatrix} = Y \quad \text{(A.103)}$$

$$\sum_{\mu=x,y,z} Y_{\tau\mu} Q(-\omega' w)_{\mu\lambda} =$$

$$= \begin{pmatrix} \cos\Omega w & \frac{\Omega}{\omega'}\sin\Omega w & \frac{\Delta}{\omega'}\sin\Omega w \\ -\frac{\Omega}{\omega'}\sin\Omega w & \frac{\Omega^2}{\omega'^2}\cos\Omega w & \frac{\Delta\Omega}{\omega'^2}\cos\Omega w \\ -\frac{\Delta}{\omega'}\sin\Omega w & \frac{\Delta\Omega}{\omega'^2}\cos\Omega w & \frac{\Delta^2}{\omega'^2}\cos\Omega w \end{pmatrix} \begin{pmatrix} \cos\omega' w & -\sin\omega' w & 0 \\ \sin\omega' w & \cos\omega' w & 0 \\ 0 & 0 & 1 \end{pmatrix} =$$

$$= \begin{pmatrix} cc' + \frac{\Omega}{\omega'}ss' & cs' - \frac{\Omega}{\omega'}sc' & -\frac{\Delta}{\omega'}s \\ \frac{\Omega}{\omega'}sc' - \frac{\Omega^2}{\omega'^2}cs' & \frac{\Omega}{\omega'}ss' + \frac{\Omega^2}{\omega'^2}cc' & \frac{\Delta\Omega}{\omega'^2}c \\ \frac{\Delta}{\omega'}sc' - \frac{\Delta\Omega}{\omega'^2}cs' & \frac{\Delta}{\omega'}ss' + \frac{\Delta\Omega}{\omega'^2}cc' & \frac{\Delta^2}{\omega'^2}c \end{pmatrix} = a(\Omega, \omega', w) \quad \text{(A.104)}$$

where $c \equiv \cos(-\Omega w)$, $s \equiv \sin(-\Omega w)$, $c' \equiv \cos(-\omega' w)$ and $s' \equiv \sin(-\omega' w)$.

Consequently, the matricial product in (4.50) is given by the matrix $a(\Omega, \omega', w)$ as defined above, while the second commutator term in (4.38) is exactly the hermitian conjugate of the first. Hence we can write the **K** operator, corrisponding to the integral in (4.38), as

$$\mathbf{K}[\tilde{\rho}_S] = -\sum_{\tau,\lambda\in\{x,m,n\}} \left(A(\Omega,\omega')_{\tau\lambda} \left[\tilde{\rho}_S\sigma^\tau, \sigma^\lambda\right] + A(\Omega,\omega')^*_{\tau\lambda}[\sigma^\lambda, \sigma^\tau\tilde{\rho}_S]\right), \quad \text{(A.105)}$$

where $A(\Omega, \omega')$ is given by

$$A(\Omega,\omega') = \int_0^{+\infty} \mathrm{d}w\, \Lambda^{-1}\tilde{R}(\Omega w)\Lambda Q(-\omega' w) G(w)^* = \int_0^{+\infty} \mathrm{d}w\, a(\Omega,\omega',w) G(w)^*. \quad \text{(A.106)}$$

Finally we write down the complete expression of the operator $\mathbf{K}$, containing both the dissipation term and the Lamb shift correction:

$$\begin{aligned}
\mathbf{K}[\tilde{\rho}_S(t)] =&\mathbf{K}\left[\frac{1}{2}(\mathbf{1}+a(t)\sigma^x+b(t)\sigma^m+c(t)\sigma^n)\right]= \\
=&-2\sigma^x\left\{a(t)\left(\frac{\Omega}{\omega'}\Re g_{ss}+\frac{\Omega^2}{\omega'^2}\Re g_{cc}+\frac{\Delta^2}{\omega'^2}\Re g_{c0}\right)+b(t)\left(-\Re g_{cs}+\frac{\Omega}{\omega'}\Re g_{sc}\right)\right. \\
&\left.+c(t)\left(\frac{\Delta}{\omega'}\Re g_{s0}\right)+\left(\frac{\Delta\Omega}{\omega'^2}\Im g_{c0}-\frac{\Delta}{\omega'}\Im g_{ss}-\frac{\Delta\Omega}{\omega'^2}\Im g_{cc}\right)\right\} \\
&-2\sigma^m\left\{a(t)\left(-\frac{\Omega}{\omega'}\Re g_{sc}+\frac{\Omega^2}{\omega'^2}\Re g_{cs}\right)+b(t)\left(\Re g_{cc}+\frac{\Omega}{\omega'}\Re g_{ss}+\frac{\Delta^2}{\omega'^2}\Re g_{c0}\right)+\right. \\
&\left.+c(t)\left(-\frac{\Delta\Omega}{\omega'^2}\Re g_{c0}\right)+\left(\frac{\Delta}{\omega'}\Im g_{s0}+\frac{\Delta}{\omega'}\Im g_{sc}-\frac{\Delta\Omega}{\omega'^2}\Im g_{cs}\right)\right\} \\
&-2\sigma^n\left\{a(t)\left(-\frac{\Delta}{\omega'}\Re g_{sc}+\frac{\Delta\Omega}{\omega'^2}\Re g_{cs}\right)+b(t)\left(-\frac{\Delta}{\omega'}\Re g_{ss}-\frac{\Delta\Omega}{\omega'^2}\Re g_{cc}\right)+\right. \\
&\left.+c(t)\left(\Re g_{cc}+2\frac{\Omega}{\omega'}\Re g_{ss}+\frac{\Omega^2}{\omega'^2}\Re g_{cc}\right)+\left(\Im g_{cs}-2\frac{\Omega}{\omega'}\Im g_{sc}+\frac{\Omega^2}{\omega'^2}\Im g_{cs}\right)\right\}
\end{aligned} \tag{A.107}$$

where we defined

$$\begin{cases}
g_{cs}=\int_0^\infty \mathrm{d}w\, G(w)\cos(-\Omega w)\sin(-\omega' w) \\
g_{sc}=\int_0^\infty \mathrm{d}w\, G(w)\sin(-\Omega w)\cos(-\omega' w) \\
g_{ss}=\int_0^\infty \mathrm{d}w\, G(w)\sin(-\Omega w)\sin(-\omega' w) \\
g_{cc}=\int_0^\infty \mathrm{d}w\, G(w)\cos(-\Omega w)\cos(-\omega' w) \\
g_{c0}=\int_0^\infty \mathrm{d}w\, G(w)\cos(-\Omega w) \\
g_{s0}=\int_0^\infty \mathrm{d}w\, G(w)\sin(-\Omega w)
\end{cases} \tag{A.108}$$

A.8. Derivation of the non-completely positive Master Equation

Here we we discuss the derivation of the master equation (4.74): we follow the so-called projection technique already shown in A.1 applied to the interaction representation. We thus set

$$R_{\mathcal{SB}}(t) = e^{it(H_{\rm eff}+H_{\mathcal{B}})/\hbar}\,\widetilde{\varrho}_{\mathcal{SB}}(t)\,e^{-it(H_{\rm eff}+H_{\mathcal{B}})/\hbar} \tag{A.109}$$

$$K_{\mathcal{SB}}(t) = e^{it(H_{\rm eff}+H_{\mathcal{B}})/\hbar}\,\widetilde{H}_{\mathcal{SB}}(t)\,e^{-it(H_{\rm eff}+H_{\mathcal{B}})/\hbar}\ , \tag{A.110}$$

whence

$$\frac{{\rm d}R_{\mathcal{SB}}(t)}{{\rm d}t} = \lambda\,\mathbb{K}_t[R_{\mathcal{SB}}(t)],\quad \mathbb{K}_t[R_{\mathcal{SB}}(t)] = -\frac{i}{\hbar}[K_{\mathcal{SB}}(t)\,,\,R_{\mathcal{SB}}(t)]. \tag{A.111}$$

Let us then introduce the following projectors acting on the space of density matrices $\widetilde{\varrho}_{\mathcal{SB}}(t)$ of the compound system $\mathcal{S}+\mathcal{B}$:

$$\mathbb{P}[R_{\mathcal{SB}}(t)] = ({\rm Tr}_{\mathcal{B}}R_{\mathcal{SB}}(t))\otimes\varrho_{\mathcal{B}} = R_t\otimes\varrho_{\mathcal{B}}\ ,\quad \mathbb{Q} = {\rm id}-\mathbb{P}\ , \tag{A.112}$$

where $\varrho_{\mathcal{B}}$ is the bath thermal state at temperature T: $[H_{\mathcal{B}}\,,\,\varrho_{\mathcal{B}}]=0$. Notice that the trace of $R_{\mathcal{SB}}(t)$ over the bath degrees of freedom,

$$R_t = {\rm Tr}_{\mathcal{B}}R_{\mathcal{SB}}(t) = e^{itH_{\rm eff}/\hbar}\,{\rm Tr}_{\mathcal{B}}\widetilde{\varrho}_{\mathcal{B}}\,e^{-itH_{\rm eff}/\hbar}\ , \tag{A.113}$$

gives the time-evolving density matrix of the open quantum system $\mathcal{S}$ in its own interaction representation.

By means of the two projections $\mathbb{P}$ and $\mathbb{Q}$ we split (A.112) into two coupled differential equations

$$\frac{{\rm d}\mathbb{P}[R_{\mathcal{SB}}(t)]}{{\rm d}t} = \lambda\,\mathbb{K}_t^{PP}\circ\mathbb{P}[R_{\mathcal{SB}}(t)] + \lambda\,\mathbb{K}_t^{PQ}\circ\mathbb{Q}[R_{\mathcal{SB}}(t)] \tag{A.114}$$

$$\frac{{\rm d}\mathbb{Q}[R_{\mathcal{SB}}(t)]}{{\rm d}t} = \lambda\,\mathbb{K}_t^{QP}\circ\mathbb{P}[R_{\mathcal{SB}}(t)] + \lambda\,\mathbb{K}_t^{QQ}\circ\mathbb{Q}[R_{\mathcal{SB}}(t)]\ , \tag{A.115}$$

where $\circ$ denotes the composition of maps, while $\mathbb{K}_t^{PP}=\mathbb{P}\circ\mathbb{K}_t\circ\mathbb{P}$, $\mathbb{K}_t^{PQ}=\mathbb{P}\circ\mathbb{K}_t\circ\mathbb{Q}$, $\mathbb{K}_t^{QP}=\mathbb{Q}\circ\mathbb{K}_t\circ\mathbb{P}$ and $\mathbb{K}_t^{QQ}=\mathbb{Q}\circ\mathbb{H}_t\circ\mathbb{Q}$. The second equation is formally solved by

$$\mathbb{Q}[R_{\mathcal{SB}}(t)] = \mathbb{W}_{t,0}^{QQ}\circ\mathbb{Q}[R_{\mathcal{SB}}] + \lambda\int_0^t{\rm d}s\,\mathbb{W}_{t,s}^{QQ}\circ\mathbb{K}_s^{QP}\circ\mathbb{P}[R_{\mathcal{SB}}(s)] \tag{A.116}$$

with the $\mathbb{W}_{t,s}^{QQ}$ the time-ordered solution of

$$\frac{{\rm d}\mathbb{W}_{t,s}^{QQ}}{{\rm d}t} = \lambda\,\mathbb{K}_t^{QQ}\circ\mathbb{W}_{t,s}^{QQ}\ ,\qquad \mathbb{W}_{s,s}={\rm id}\ . \tag{A.117}$$

By choosing as initial condition $\widetilde{\varrho}_{\mathcal{SB}}=\varrho\otimes\varrho_{\mathcal{B}}$ yields $\mathbb{Q}[R_{\mathcal{SB}}]=\mathbb{Q}[\widetilde{\varrho}_{\mathcal{SB}}]=0$ whence

$$\mathbb{Q}[R_{\mathcal{SB}}(t)] = \lambda\int_0^t{\rm d}s\,\mathbb{W}_{t,s}^{QQ}\circ\mathbb{K}_s^{QP}\circ\mathbb{P}[R_{\mathcal{SB}}(s)]\ . \tag{A.118}$$

Once inserted into (A.114), this provides a master equation involving $\mathbb{P}[R_{\mathcal{SB}}(t)]$ alone:

$$\frac{\mathrm{d}\mathbb{P}[R_{\mathcal{SB}}(t)]}{\mathrm{d}t} = \lambda\,\mathbb{K}_t^{PP}\circ\mathbb{P}[R_{\mathcal{SB}}(t)] + \lambda^2\int_0^t \mathrm{d}s\,\mathbb{K}_t^{PQ}\circ\mathbb{W}_{t,s}^{QQ}\circ\mathbb{H}_s^{QP}\circ\mathbb{P}[R_{\mathcal{SB}}(s)]\ . \quad \text{(A.119)}$$

Because of the action of $\mathbb{P}$ in (A.111), of the form of the interaction Hamiltonian and of the fact that, with $\varrho_{\mathcal{B}}$ a thermal Gibbs state, the position operators have vanishing mean values, one gets $\mathrm{Tr}_{\mathcal{B}}\Big(\varrho_{\mathcal{B}}K_{\mathcal{SB}}(t)\Big) = 0$. Therefore, from $\mathbb{P}[R_{\mathcal{SB}}(t)] = R_t\otimes\varrho_{\mathcal{B}}$, one gets

$$\frac{\mathrm{d}R_t}{\mathrm{d}t} = -\frac{\lambda^2}{\hbar^2}\int_0^t \mathrm{d}u\,\mathrm{Tr}_{\mathcal{B}}\Big(\Big[K_{\mathcal{SB}}(t),\mathbb{Q}\circ\mathbb{W}_{t,u}^{QQ}\circ\mathbb{Q}\Big[K_{\mathcal{SB}}(u)\,,\,R_u\otimes\varrho_{\mathcal{B}}\Big]\Big]\Big)\ . \quad \text{(A.120)}$$

The above equation depends on the history of the system $\mathcal{S}$ state R_s for all times $0\leq s\leq t$; in order to eliminate this dependence, one takes into account the weak-coupling hypothesis $\lambda\ll 1$ and looks at the dynamics as a function of a slow time parameter $\tau = t\lambda^2$. Firstly, by a change of integration variable $s = t-u$, (A.120) is recast as

$$\frac{\mathrm{d}R_t}{\mathrm{d}t} = -\frac{\lambda^2}{\hbar^2}\int_0^t \mathrm{d}u\,\mathrm{Tr}_{\mathcal{B}}\Big(\Big[K_{\mathcal{SB}}(t),\mathbb{Q}\circ\mathbb{W}_{t,t-u}^{QQ}\circ\mathbb{Q}\Big[K_{\mathcal{SB}}(t-u)\,,\,R_{t-u}\otimes\varrho_{\mathcal{B}}\Big]\Big]\Big)\ . \quad \text{(A.121)}$$

Then, letting $\lambda\to 0$, $\mathbb{W}_{t,s}^{QQ}\to\mathrm{id}$ for the right hand side in (A.111) is proportional to λ, and

$$\mathbb{Q}\circ\mathbb{W}_{t,s}^{QQ}\circ\mathbb{Q}\Bigg[\Big[K_{\mathcal{SB}}(s)\,,\,R_s\otimes\varrho_{\mathcal{B}}\Big]\Bigg]\to\mathbb{Q}\Bigg[\Big[K_{\mathcal{SB}}(s)\,,\,\widetilde{\varrho}_s\otimes\varrho_{\mathcal{B}}\Big]\Bigg] = \Big[K_{\mathcal{SB}}(s)\,,\,\widetilde{\varrho}_s\otimes\varrho_{\mathcal{B}}\Big]\ ,$$

where the last equality follows since, as explained before, the bath operators have vanishing mean-values with respect to the thermal state $\varrho_{\mathcal{B}}$.

At this point, one usually sends the integration upper limit to $+\infty$ and replaces $t-u=\tau/\lambda^2-u$ with t in R_{t-u} whence the second term on the right hand side of (A.121) reads

$$\mathbb{D}_t[R_t] = -\frac{\lambda^2}{\hbar^2}\int_0^{+\infty}\mathrm{d}u\,\mathrm{Tr}_{\mathcal{B}}\Big(\Big[K_{\mathcal{SB}}(t)\,,\,\Big[K_{\mathcal{SB}}(t-u)\,,\,R_t\otimes\varrho_{\mathcal{B}}\Big]\Big]\Big)\ . \quad \text{(A.122)}$$

By going back to the initial picture, one gets the following master equation for $\widetilde{\varrho}_t$,

$$\frac{\mathrm{d}\widetilde{\varrho}_t}{\mathrm{d}t} = -\frac{i}{\hbar}\Big[H_{\mathrm{eff}}\,,\,\widetilde{\varrho}_t\Big] + \lambda^2\,\widetilde{\mathbb{D}}_t[\widetilde{\varrho}_t] \quad \text{(A.123)}$$

$$\widetilde{\mathbb{D}}_t[\widetilde{\varrho}_t] = -\frac{1}{\hbar^2}\int_0^{+\infty}\mathrm{d}u\,\mathrm{Tr}_{\mathcal{B}}\Big(\Big[\widetilde{H}_{\mathcal{SB}}(t)\,,\,\Big[\mathrm{e}^{u(\mathbb{H}_{\mathrm{eff}}+\mathbb{H}_{\mathcal{B}})}[\widetilde{H}_{\mathcal{SB}}(t-u)]\,,\,\widetilde{\varrho}_t\otimes\varrho_{\mathcal{B}}\Big]\Big]\Big)_{,} \quad \text{(A.124)}$$

where

$$\mathrm{e}^{u(\mathbb{H}_{\mathrm{eff}}+\mathbb{H}_{\mathcal{B}})}[X] = \mathrm{e}^{-iu(H_{\mathrm{eff}}+H_{\mathcal{B}})/\hbar}\,X\,\mathrm{e}^{iu(H_{\mathrm{eff}}+H_{\mathcal{B}})/\hbar}\ . \quad \text{(A.125)}$$

It is immediate to recognize that the operator $\widetilde{\mathbb{D}}_t$ corresponds to the $\mathbf{K}_1$ operator in the classification of the different Markovian approximation that we discussed in sec. 5. Moreover, by substituting the interaction Hamiltonian with its expression (4.10) and after calculating the trace as in sec. A.7, one can easily show that $\widetilde{\mathbb{D}}_t$ is exactly the integral operator in (4.74).

A.9. Violations of the positivity requirement

We want to show that the dynamical semigroup given by

$$\gamma_t[\rho] \equiv e^{t\mathbf{L}}[\rho] \tag{A.126}$$

$$\mathbf{L}[\rho] \equiv -i\,[H_{\text{eff}}, \rho] + \mathbf{K}[\rho] \tag{A.127}$$

with $\mathbf{K} = \mathbf{K}_1$, from eq. (4.78), is not even a positive map, for certain values of the parameters Ω, ω'.

We look for a pure state $|\psi\rangle\langle\psi|$ such that its evoluted state breaks positivity at first order in t. To be precise, given

$$|\psi\rangle\langle\psi| \mapsto \gamma_t[|\psi\rangle\langle\psi|] = |\psi\rangle\langle\psi| + t\mathbf{L}[|\psi\rangle\langle\psi|] + \mathcal{O}(t^2), \tag{A.128}$$

we can construct a state $|\phi\rangle$ which shows the non-positivity of the map γ_t, in the sense that it violates

$$\begin{aligned} 0 \leq \langle\phi\,|\,\psi\rangle\langle\psi\,|\,\phi\rangle + t\,\langle\phi\,|\,\mathbf{L}[|\psi\rangle\langle\psi|]\,|\,\phi\rangle + \mathcal{O}(t^2) = \\ = |\langle\phi\,|\,\psi\rangle|^2 + t\,\langle\phi\,|\,\mathbf{L}[|\psi\rangle\langle\psi|]\,|\,\phi\rangle + \mathcal{O}(t^2). \end{aligned} \tag{A.129}$$

Since the source of negativity in the above expression can only come from the term proportional to t, we choose $|\phi\rangle \perp |\psi\rangle$, so that

$$\begin{aligned} \langle\phi\,|\,\mathbf{L}[|\psi\rangle\langle\psi|]\,|\,\phi\rangle &= \langle\phi\,|\,\mathbf{K}[|\psi\rangle\langle\psi|]\,|\,\phi\rangle = \\ &= \langle\phi\,|\,V_1\,|\,\psi\rangle\left\langle\psi\,\middle|\,V_2^\dagger\,\middle|\,\phi\right\rangle + \langle\phi\,|\,V_2\,|\,\psi\rangle\left\langle\psi\,\middle|\,V_1^\dagger\,\middle|\,\phi\right\rangle + \\ &\quad + \langle\phi\,|\,V_3\,|\,\psi\rangle\left\langle\psi\,\middle|\,V_4^\dagger\,\middle|\,\phi\right\rangle + \langle\phi\,|\,V_4\,|\,\psi\rangle\left\langle\psi\,\middle|\,V_3^\dagger\,\middle|\,\phi\right\rangle. \end{aligned} \tag{A.130}$$

Now, we have already seen that the Master Equation (4.74), expressed in the rotated frame of reference, is actually time-independent, and therefore the Lindblad operators (4.77) can be evaluated at any time, for example at $t = 0$. In particular $V_2 = \sigma^z = V_2^\dagger$ and $V_4 = \sigma^x = V_4^\dagger$.

With the parametrization

$$|\psi\rangle = \frac{1}{\sqrt{1+|\xi|^2}}\begin{pmatrix}1\\ \xi\end{pmatrix}, \quad |\phi\rangle = \frac{1}{\sqrt{1+|\xi|^2}}\begin{pmatrix}-\xi^*\\ 1\end{pmatrix}, \qquad \xi = |\xi|e^{i\arg\xi} \in \mathbb{C}, \tag{A.131}$$

we have

$$\langle\psi\,|\,\sigma^z\,|\,\phi\rangle = -\frac{2\xi^*}{1+|\xi|^2}, \quad \langle\psi\,|\,\sigma^n\,|\,\phi\rangle = \frac{1-\xi^{*2}}{1+|\xi|^2}. \tag{A.132}$$

Then, by defining

$$\gamma_1 \equiv \langle\phi\,|\,V_1\,|\,\psi\rangle\,, \quad \gamma_3 \equiv \langle\phi\,|\,V_3\,|\,\psi\rangle\,, \tag{A.133}$$

we obtain

$$0 \le \langle\phi\,|\,\mathbf{K}[|\psi\rangle\,\langle\psi|]\,|\,\phi\rangle = \frac{2}{1+|\xi|^2}\Re\left\{\gamma_1(-2\xi^*) + (1-\xi^{*2})\gamma_3\right\}, \tag{A.134}$$

where

$$\gamma_1 = \frac{1}{1+|\xi|^2}\left(-\xi V_{1(00)} + V_{1(10)} - \xi^2 V_{1(01)} + \xi V_{1(11)}\right), \tag{A.135}$$

$$\gamma_3 = \frac{1}{1+|\xi|^2}\left(-\xi V_{3(00)} + V_{3(10)} - \xi^2 V_{3(01)} + \xi V_{3(11)}\right), \tag{A.136}$$

$V_{1(ij)}$, $V_{3(ij)}$, being the matrix components of V_1, V_3 in the basis $\{|0\rangle\,, |1\rangle\}$.

Consequently, the positivity condition (A.129), is expressed by

$$\begin{aligned} 0 \le \Re\Big\{&\left(2|\xi|^2 V_{1(00)} - 2\xi^* V_{1(10)} + 2|\xi|^2\xi V_{1(01)} - 2|\xi|^2 V_{1(11)}\right) + \\ &+ \left(-\xi V_{3(00)} + V_{3(10)} - \xi^2 V_{3(01)} + \xi V_{3(11)}\right) + \\ &+ \left(|\xi|^4 V_{3(01)} + |\xi|^2\xi^* V_{3(00)} - |\xi|^2\xi^* V_{3(11)} - \xi^{*2} V_{3(10)}\right)\Big\}, \end{aligned} \tag{A.137}$$

for all $\xi \in \mathbb{C}$.

We are interested in the sign of the coefficient of the highest power of $|\xi|$, $V_{3(01)}$.

$$V_{3(01)} = \sum_{j,k=0,1}\int_0^\infty \mathrm{d}t\, G(\tau)U_0^\dagger(-\tau)_{0j}\tilde{\sigma}^x(-\tau)_{jk}U_0(-\tau)_{k1}. \tag{A.138}$$

The integrand can be worked out after evaluating $\tilde{\sigma}^x(-\tau)$:

$$\tilde{\sigma}^x(-\tau) = R_y^{-1}(-\Omega\tau)\sigma^x R_y(-\Omega\tau) = e^{-i\frac{\Omega\tau}{2}\sigma^y}\sigma^x e^{i\frac{\Omega\tau}{2}\sigma^y} = \sigma^x\cos\Omega\tau - \sigma^z\sin\Omega\tau, \tag{A.139}$$

and then[1]

$$
\begin{aligned}
U_0^\dagger(-\tau)\tilde{\sigma}^x(-\tau)U_0(-\tau) &= e^{-i\frac{\omega'}{2}\sigma^n\tau}(\sigma^x\cos\Omega\tau - \sigma^z\sin\Omega\tau)e^{i\frac{\omega'}{2}\sigma^n\tau} = \\
&= \left(\cos\omega'\tau\cos\Omega\tau + \frac{\Omega}{\omega'}\sin\omega'\tau\sin\Omega\tau\right)\sigma^x + \\
&\quad + \left(\sin\omega'\tau\cos\Omega\tau - \frac{\Omega}{\omega'}\cos\omega'\tau\sin\omega'\tau\right)\sigma^m - \frac{\Delta}{\omega'}\sigma^n = \\
&= \left(\cos\omega'\tau\cos\Omega\tau + \frac{\Omega}{\omega'}\sin\omega'\tau\sin\Omega\tau\right)\sigma^x + \\
&\quad + \left(\frac{\Delta}{\omega'}(\sin\omega'\tau\cos\Omega\tau - \frac{\Omega}{\omega'}\cos\omega'\tau\sin\Omega\tau) + \frac{\Delta\Omega}{\omega'^2}\sin\Omega\tau\right)\sigma^y + \\
&\quad + f(\Omega,\omega',\tau)\sigma^z.
\end{aligned}
$$

We study the sign of $|\xi|^4\Re V_{3(01)}$

$$
\begin{aligned}
\Re V_{3(01)} = &\int_0^{+\infty} \mathrm{d}\tau\,\Re G(\tau)\left(\cos\omega'\tau\cos\Omega\tau + \frac{\Omega}{\omega'}\sin\omega'\tau\sin\Omega\tau\right) + \\
&+ \int_0^{+\infty} \mathrm{d}\tau\,\Im G(\tau)\left(\frac{\Delta}{\omega'}\sin\omega'\tau\cos\Omega\tau - \frac{\Delta\Omega}{\omega'^2}\cos\omega'\tau\sin\Omega\tau + \frac{\Delta\Omega}{\omega'^2}\sin\Omega\tau\right) = \\
&= \Re g_{cc} + \frac{\Omega}{\omega'}\Re G_{ss} - \frac{\Delta}{\omega'}\Im g_{cs} - \frac{\Delta\Omega}{\omega'^2}\Im g_{sc} - \frac{\Delta\Omega}{\omega'^2}\Im g_{s0} = \\
&= \frac{\alpha\pi}{4}\Bigg\{(\omega'+\Omega)e^{-\frac{\omega'+\Omega}{\omega_c}}\coth\frac{\beta(\omega'+\Omega)}{2} + (\omega'-\Omega)e^{-\frac{\omega'-\Omega}{\omega_c}}\coth\frac{\beta(\omega'-\Omega)}{2} + \\
&- \frac{\Omega}{\omega'}\left((\omega'+\Omega)e^{-\frac{\omega'+\Omega}{\omega_c}}\coth\frac{\beta(\omega'+\Omega)}{2} - (\omega'-\Omega)e^{-\frac{\omega'-\Omega}{\omega_c}}\coth\frac{\beta(\omega'-\Omega)}{2}\right) + \\
&- \frac{\Delta}{\omega'}\left((\omega'+\Omega)e^{-\frac{\omega'+\Omega}{\omega_c}} - (\omega'-\Omega)e^{-\frac{\omega'-\Omega}{\omega_c}}\right) + \\
&- \frac{\Delta\Omega}{\omega'^2}\left((\omega'+\Omega)e^{-\frac{\omega'+\Omega}{\omega_c}} - (\omega'-\Omega)e^{-\frac{\omega'-\Omega}{\omega_c}}\right)\Bigg\} - \frac{\Delta\Omega}{\omega'^2}\Im g_{s0}.
\end{aligned} \tag{A.140}
$$

[1]The σ^z coefficient, $f(\Omega,\omega',\tau)$, is irrelevant in the calculation of (A.138), because the (01) element appears only in σ^x and σ^y.

$\Im g_{s0}$ is given by:

$$\begin{aligned}
\Im g_{s0} &= \int_0^{+\infty} \mathrm{d}\tau\ \sin(-\Omega\tau)\Im G(\tau) = \\
&= \int_0^{+\infty} \mathrm{d}\tau\ \sin(-\Omega\tau) \int_0^{+\infty} \mathrm{d}k\, \alpha k e^{-k/\omega_c} \Im\{\cos k\tau \coth\frac{\beta k}{2} - i\sin k\tau\} = \\
&= \alpha \int_0^{+\infty} \mathrm{d}k\, k e^{-k/\omega_c} \int_0^{+\infty} \mathrm{d}\tau\ \sin\Omega\tau \sin k\tau = \\
&= -\frac{\alpha\pi}{4} \int_0^{+\infty} \mathrm{d}k\, 2k e^{-k/\omega_c} \left(\delta(k+\Omega) - \delta(k-\Omega)\right) = \\
&= \frac{\pi\alpha}{2}\Omega \left(e^{-\frac{\Omega}{\omega_c}} - e^{\frac{\Omega}{\omega_c}}\right).
\end{aligned} \tag{A.141}$$

We can study the limit $\Omega \to \infty$ but we must also impose how ω', which is always greater than Ω, goes to infinity. For example we could impose that the ratio Ω/ω' remains constant and let $\omega' \to \infty$. It's evident that this implies that $\coth\frac{\beta(\omega'\pm\Omega)}{2} \xrightarrow{\omega'\to\infty} 1$ while the exponentials $e^{-\frac{\omega'\pm\Omega}{\omega_c}}$ kill all the terms but the last one in (A.140)

$$-\frac{\Delta\Omega}{\omega'^2}\Im g_{s0} = -\frac{\pi\Delta\alpha}{2}\frac{\Omega^2}{\omega'^2}\left(e^{-\Omega/\omega_c} - e^{\Omega/\omega_c}\right) \xrightarrow{\omega'\to\infty} +\infty. \tag{A.142}$$

This means that even if we increase ξ in (A.131) in order to make the $|\xi|^4$ term dominate, we cannot ensure the positivity violation for large Ω, because its coefficient goes to ∞.

But in the same way we can show that the zero order term, independent from ξ, which is $\Re V_{3(10)}$, is increasily negative in the same limit for Ω, ω'. Indeed

$$\begin{aligned}
\Re V_{3(10)} = &\int_0^{+\infty} \mathrm{d}\tau \Re\left\{G(\tau)\left[U_0^\dagger(-\tau)\tilde{\sigma}^x(-\tau)U_0(-\tau)\right]_{10}\right\} = \\
&= \int_0^{+\infty} \mathrm{d}\tau \Re\left\{G(\tau)\left[\cos\omega'\tau\cos\Omega\tau + \frac{\Omega}{\omega'}\sin\omega'\tau\sin\Omega\tau + \right.\right. \\
&\left.\left. +i\left(\frac{\Delta}{\omega'}\left(\sin\omega'\tau\cos\Omega\tau - \frac{\Omega}{\omega'}\cos\omega'\tau\sin\Omega\tau\right) + \frac{\Delta\Omega}{\omega'^2}\sin\Omega\tau\right)\right]\right\} = \\
&= \Re g_{cc} + \frac{\Omega}{\omega'}\Re G_{ss} + \frac{\Delta}{\omega'}\Im g_{cs} + \frac{\Delta\Omega}{\omega'^2}\Im g_{sc} + \frac{\Delta\Omega}{\omega'^2}\Im g_{s0},
\end{aligned} \tag{A.143}$$

where the sign is inverted.

Consequently, if we choose $\xi = 0$ in (A.131), i.e.

$$|\psi\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, |\phi\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \tag{A.144}$$

then

$$\langle \phi \,|\, \mathbf{L}[|\psi\rangle \langle\psi|] \,|\, \phi\rangle \xrightarrow{\Omega,\omega'\to\infty} -\infty. \tag{A.145}$$

So one can conclude that there certainly exist pure states that are mapped by the dynamics $\gamma_t = e^{t\mathbf{L}}$ generated by the M.E. proposed in [31], into density matrices $\gamma_t[|\psi\rangle\langle\psi|]$ which are non-positive, hence non-physical, for some suitable values of the parameters Ω, ω'.

A.10. Explicit expression of the original Master Equation

In this section we report for convenience the explicit form of the Master Equation proposed by Tosatti et al. in[31]:

$$\begin{aligned}
\frac{\partial\tilde{\rho}_S(t)}{\partial t} = -2\Bigg\{&\frac{\Delta}{\omega'}\Bigg(-\frac{\Omega}{\omega'}\Re g_{c0} + \Im g_{ss} + \frac{\Omega}{\omega'}\Im g_{cc}\Bigg) + \Bigg(\frac{\Delta^2}{\omega'^2}\Re g_{c0} + \frac{\Omega}{\omega'}\Re g_{ss} + \frac{\Omega^2}{\omega'^2}\Re g_{cc}\Bigg)a + \\
&\Bigg(\frac{\omega'}{4} + \frac{\Omega}{\omega'}\Re g_{sc} - \frac{\Omega^2}{\omega'^2}\Re g_{cs}\Bigg)b + \frac{\Delta}{\omega'}\Bigg(\Re g_{sc} - \frac{\Omega}{\omega'}\Re g_{cs}\Bigg)c\Bigg\}\sigma_x + \\
-2\Bigg\{&\frac{\Delta}{\omega'}\Bigg(\Im g_{s0} + \Im g_{sc} - \frac{\Omega}{\omega'}\Im g_{cs}\Bigg) + \Bigg(-\frac{\omega'}{4} - \frac{\Omega}{\omega'}\Re g_{sc} + \Re g_{cs}\Bigg)a + \\
&\Bigg(\frac{\Delta^2}{\omega'^2}\Re g_{c0} + \Re g_{cc} + \frac{\Omega}{\omega'}\Re g_{ss}\Bigg)b - \frac{\Delta}{\omega'}\Bigg(\Im g_{s0} + \Im g_{sc} - \frac{\Omega}{\omega'}\Im g_{cs}\Bigg)c\Bigg\}\sigma_m + \\
-2\Bigg\{&\Bigg(-2\frac{\Omega}{\omega'}\Im g_{sc} + \frac{\Omega^2+\omega'^2}{\omega'^2}\Im g_{cs}\Bigg) - \frac{\Delta}{\omega'}\Re g_{s0}a + \\
&-\frac{\Omega\Delta}{\omega'^2}\Re g_{c0}b + \Bigg(\frac{\Omega^2+\omega'^2}{\omega'^2}\Re g_{cc} + 2\frac{\Omega}{\omega'}\Re g_{ss}\Bigg)c\Bigg\}\sigma_n\,.
\end{aligned} \tag{A.146}$$

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