QUANTUM THERMODYNAMICS: A BRIEF INTRODUCTION TO QUANTUM THERMAL MACHINES

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Trabajo Fin de Grado

Septiembre 2020

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Acknowledgements

A mis familiares y amigos, por su apoyo absoluto en los momentos más difíciles.

A mi profesor de secundaria, Juan Jesús, por hacerme ver que la Física era una ciencia extraordinaria.

A Daniel por su gran ayuda y conocimientos transmitidos en la labor de este proyecto.

A mis abuelos, que no pudieron ver este gran logro.

Resumen/Abstract

Resumen

El objetivo de traer al lector una revisión académica simple del importante reciente campo de investigación de la Termodinámica cuántica es el eje central de este proyecto. Para conseguirlo nos centramos en las máquinas térmicas cuánticas. Una introducción a este importante tema es presentado junto al concepto de máquinas térmicas endoreversibles. En primer lugar, mostramos un estudio de su rendimiento motivado por un modelo cuántico: Un Maser de tres niveles junto a unos resultados muy interesantes de su comportamiento. Posteriormente, con la idea de entender como funciona la dinámica de estos dispositivos nos moveremos a la teoría de sistemas cuánticos abiertos mostrando la derivación de una herramienta matemática muy importante en el campo de la Termodinámica cuántica: La ecuación maestra Markoviana. Para finalizar, aplicaremos esta ecuación a un sistema específico observando como la primera y segunda ley de la termodinámica emergen de su dinámica.

Abstract

The purpose of bring the reader and academical and modest review of the emerging research field of Quantum Thermodynamics is the central axis of this project. To do that we focus on quantum thermal machines. An introduction to this important subject is addressed along with the notion of endoreversible thermal machines. First, we present a study of thermal devices performance utilizing a particular quantum model: The Three Level Maser, from which rather general results can be derived. The idea is to understand in simple terms how the

dynamics of this type of systems works. Later, we will introduce some basic elements of the theory of open quantum systems showing the derivation of an important mathematical tool in Quantum Thermodynamics: The Markovian master equation ruling the reduce dynamics of the system of interest. To finish, we apply this equation to an specific system and see how the I-law and II-law of thermodynamics emerge in this context.

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Chapter 1

Introduction and motivation

In 1824, the French military engineer Sadi Carnot, in his single work [1], developed a reversible ideal thermal machine (the Carnot cycle) that established the maximum efficiency attainable by heat engines.

This investigation leads, years later, to the origin of thermodynamics: The I and II law. However, this thermal machine is an idealization. Real devices as cars or generating stations operates far from the maximum efficiency stablished in Carnot's studies. What happens if we optimize the operations of these devices in terms of power delivered? Or if we include a description of irreversibility in our machines? This type of questions triggered the birth of finite-time thermodynamics and the origin of endoreversible models of thermal devices [2–4].

Thermodynamics progressed with many new discoveries, collected in reference [5]. Einstein, in 1905, inspired by the Planck's ideas about thermodynamics of black body radiation, quantized the electromagnetic field [6]. This fact supposed the dawn of one of the most successfully and surprising theories in Physics: quantum mechanics. Apart from that, incidentally, the birth of quantum thermodynamics took place. The theory of quantum mechanics developed separately from thermodynamics, with its own experiments and hypothesis [7].

In 1959, Scovil and Schulz-DuBois, decided to unify this beautiful theories again in a fundamental paper on quantum thermodynamics [8]. They create the prime example of a

quantum thermal machine (QTM), the three level maser and study how thermodynamics laws emerge from a quantum system. In the next years more models of QTM's were studied [9, 10]. Two important keys in quantum thermodynamics are the theory of open quantum systems [11] and the Markovian master equation started by the work of Lindblad and Gorini-Kossakowski-Sudarshan [12, 13].

However, the term quantum thermodynamics was introduced for the first time in 1989 by Partovi [14]. That is why we say that quantum thermodynamics is an emerging research field whose main objective is to find consistency between thermodynamics laws and quantum physics. Quantum thermodynamics is a multidisciplinary field because it is based in different research areas such as Statiscal Physics, Many-body theory and quantum information theory. In reference [15] a complete description about quantum thermodynamics is given and many of the most important aspects of this field are discussed.

Quantum thermal machines is an important topic within quantum thermodynamics. Actually, many studies of this field are focused on the performance of continuous thermal machines [16–21] and internal heat leaks in quantum thermodynamic cycles [22] to reanalyze in different ways QTM's that have been studied in the past [23, 24]. Because of this, QTM's are gonna be the central axis of our study.

This work aims to review in simple terms some of the goals in quantum thermodynamics in the context of thermal devices. We shall also introduce some basic tools in the theory of open quantum systems. In Chapter 2, we start studying endoreversible thermal machines giving, in the first place, an introduction to this type of device. Then we move our attention to the performance of a specific endoreversible QTM: The Three Level Maser. In Chapter 3 we review the theory of open quantum systems and made a detailed derivation of a mathematical one of the most common tools used in quantum thermodynamics: Markovian master equations. In Chapter 4, we obtain the heat currents in the steady state of a quantum Tricycle as an example of the application of our Markovian master equation. Finally, the main conclusions of our work are drawn in Chapter 5.

Chapter 2

Endoreversible thermal machines

A Carnot engine is a thermal engine that operates reversibly extracting energy characterized by an energy current J_h from a heat bath at temperature T_h to transform it in useful power P. In that process, an amount energy with associate current J_c is delivered to a cold bath at temperature T_c. The principles of Thermodynamics impose that the efficiency η of a thermal engine has an upper bound given by the Carnot theorem

$$\eta = \frac{P}{J_h} \leqslant \quad \eta_C \quad = 1 - \frac{T_c}{T_h}. \tag{2.1}$$

This limit is far away from reality and from a practical point of view because to reach maximum efficiency, a reversible process with infinitely slow operation its required. This implies that output power is zero. In real engines many sources of irreversibility has to be considered. This problem gave rise to endoreversible thermodynamics and finite-time thermodynamics.

Let us mention that considerations leading to endoreversible thermodynamics are due to the pionering works of Novikov and Chambdal [2, 3], in the context of atomic power plants and to Curzon and Ahlborn [4].

First, we will focus on the Curzon-Alhborn (CA) endoreversible thermal machine [4] and introduce the CA efficiency following a similar procedure to the one introduced in [25]. After we move our attention to the three-level maser machine and its properties [8, 16, 24].

In this context we will introduce a simple optimization problem *i.e.*, the evaluation of the efficiency of the machine at maximum power, following the steps of reference [17] and discuss its universallity properties [26].

2.1   Curzon-Ahlborn efficiency

The Curzon and Ahlborn model depicted in (Figure 2.1) uses an endoreversible approximation that consist in include only irreversibility associated with the imperfect thermal contact between the working fluid and the heat reservoirs at temperatures T_h and T_c. This working fluid follows an internal Carnot Cycle operating at temperatures T_H and T_C, that are understood as the effective temperatures of this fluid at the hot and the cold terminals of the cycle, respectively [4, 25]. Note that in endoreversible models other sources of irreversibility, as internal friction or heat leaks, are neglected. Curzon and Ahlborn obtained that the efficiency at maximum power was given by

$$\eta_{CA} = 1 - \sqrt{\frac{T_c}{T_h}}. \tag{2.2}$$

This expression can be proven in several ways. Here, we give a simple derivation. The heat currents are given by the Newton's law of cooling between the thermal reservoirs and the effective temperatures of the working fluid, *i.e.*

$$
\begin{aligned}
J_h &= \alpha_h(T_h - T_H) = \alpha_h y_h \\
J_c &= \alpha_c(T_c - T_C) = \alpha_h y_c
\end{aligned}
\tag{2.3}
$$

where α_h and α_c are constants depending on the thermal conductivity associated to the heat fluxes. The parameters $y_h = T_h - T_H \geqslant 1$ and $y_c = T_c - T_C \leqslant 1$ are introduce for later convenience.

As previously mentioned, the internal engine follows a Carnot Cycle. Due to this, it obeys
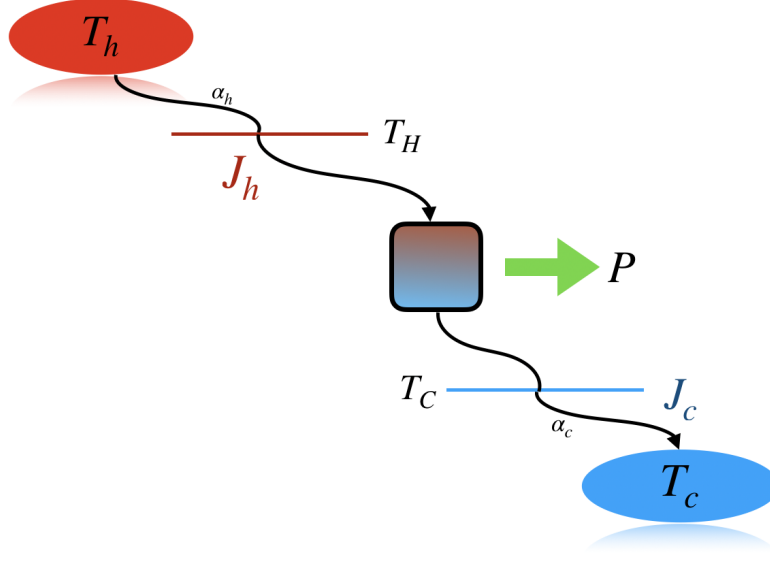
Figure 2.1: *Endoreversible model or CA cycle*

the Clausius equality:

$$\frac{J_h}{T_H} = \frac{J_c}{T_C}. \tag{2.4}$$

This last expression establishes a relation between y_c and y_h. Using equation 2.3, it follows:

$$y_h = \frac{T_h y_c}{T_c \alpha_{hc} + y_c(1 - \alpha_{hc})} \tag{2.5}$$

with $\alpha_{hc} = \frac{\alpha_h}{\alpha_c}$. The output power defined by $P \equiv \dot{Q}_h - \dot{Q}_c = \alpha_h y_h - \alpha_c y_c$ can be rewritten using 2.5 as:

$$P = \frac{T_h \alpha_{hc} y_c}{T_c \alpha_{hc} + y_c(1 - \alpha_{hc})} - y_c, \tag{2.6}$$

which shows that for fixed values of temperatures T_h, T_c and the heat conductivity parameters, the power only depends on y_c. Precisely, the optimization problem to be considered is the optimization of power with respect to this variable, *i.e.*, $\left(\frac{dP}{dy_c}\right)_{y_c=y_{c_{op}}} = 0$. Solving this equation, the optimal parameters y_c and y_h are given by:

$$
\begin{aligned}
y_{c_{op}} &= \frac{T_c \alpha_{hc} + \alpha_{hc}\sqrt{T_c T_h}}{\alpha_{hc} - 1}. \\
y_{h_{op}} &= -\frac{T_h(T_c + \sqrt{T_c T_h})}{\sqrt{T_c T_h}(\alpha_{hc} - 1)},
\end{aligned}
\tag{2.7}
$$

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from which follows the maximum power output and the efficiency $\eta = \frac{P}{J_h}$ at maximum power, *i.e.*

$$
\begin{aligned}
P_{max} &= -\frac{\alpha_{hc}}{\sqrt{T_c T_h}(\alpha_{hc}-1)}(2T_c T_h + T_c\sqrt{T_c T_h} + T_h\sqrt{T_c T_h}) \\
\eta_{maxP} &= \frac{P_{max}}{J_h(y_{h_{op})}} = 1 - \sqrt{\frac{T_c}{T_h}} = \eta_{CA}.
\end{aligned}
\tag{2.8}
$$

In terms of the Carnot efficiency (2.1) we can write the Curzon-Alhborn efficiency as

$$
\eta_{CA} = 1 - \sqrt{1-\eta_C}
\tag{2.9}
$$

and performing a Taylor expansion in η_C we obtain that

$$
\eta_{CA} = \frac{\eta_C}{2} + \frac{\eta_C^2}{8} + O(\eta_C^3).
\tag{2.10}
$$

This expression has an universal character . At linear response or at linear order in η_C many models of heat engines, both classical and quantum, show that its efficiency is limited by the linear term of CA efficiency Taylor expansion (2.10). Moreover, even in strong coupling models with left right symmetry the universality at quadratic order is achieved. In reference [26] this universality is discussed and in next section we shall see that for a type of QHE: "The three level Maser", the universality of the efficiency at maximum power in linear response regime.

2.2   The three level Maser

The three level maser, also commonly called as three level amplifier, is an endoreversible quantum thermal machine that uses population inversion between levels to obtain useful power and therefore operate as a heat engine, or alternatively, changing its operation mode it works as a refrigerator. This device was first studied by Scovil and Schulz-Dubois in [8], a very influential work in the development of quantum thermodynamics and its related subject quantum thermal machines (QTM). The thermodynamics of the level maser has

been discussed in many references [16, 17, 24, 27], and some physical implementations have been introduced, for instance in [23], where the three level system is introduced in a optical cavity. In this chapter we are going to focus our attention on the optimal operation of a three level maser, following closely the discussion made in [17].

The device, showed in Figure 2.2, is compose by a three level quantum system that acts as a "thermodynamic working fluid", coupled via a frequency filter to unstructured bosonic baths with temperatures T_c and T_h. Furthermore, we are considering here that the system is periodically driven by a laser of frequency Ω tuned to the Bohr frequency between hot and cold levels.
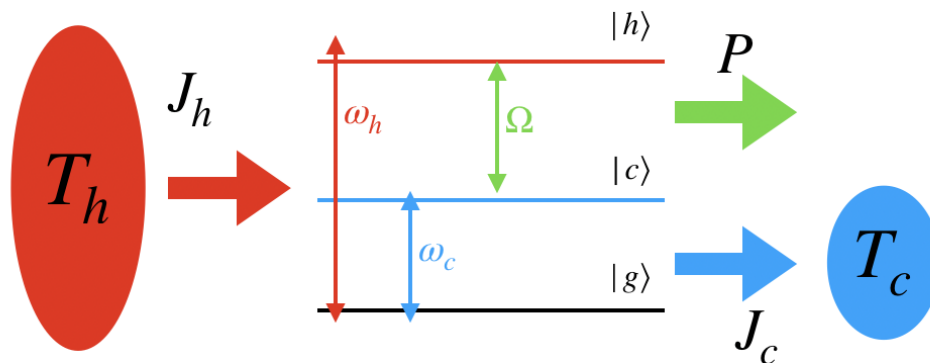
Figure 2.2: *Structure of the three level system*

The population of each level is given by

$$p_i = \frac{e^{-\beta E_i}}{Z} \tag{2.11}$$

and in natural units ($\hbar = k_B = 1$), the quotient between populations are

$$\frac{p_h}{p_g} = e^{-\beta(E_h - E_g)} = e^{-\frac{\omega_h}{T_h}} \quad \text{and} \quad \frac{p_c}{p_g} = e^{-\beta(E_c - E_g)} = e^{-\frac{\omega_c}{T_c}}. \tag{2.12}$$

We define the gain as $G = p_h - p_c$. In terms of its sign we can have a thermal engine ($G \geqslant 0$)

or a thermal refrigerator ($G \leqslant 0$). Dividing G by p_g and using equations 2.12 it follows the conditions:

Engine

$$e^{-\frac{\omega_h}{T_h}} - e^{-\frac{\omega_c}{T_c}} \geqslant 0 \longrightarrow e^{\frac{\omega_c}{T_c}} - e^{\frac{\omega_h}{T_h}} \geqslant 0 \longrightarrow \frac{\omega_c}{\omega_h} \geqslant \frac{T_c}{T_h}. \tag{2.13}$$

Refrigerator

$$e^{-\frac{\omega_h}{T_h}} - e^{-\frac{\omega_c}{T_c}} \leqslant 0 \longrightarrow e^{\frac{\omega_c}{T_c}} - e^{\frac{\omega_h}{T_h}} \leqslant 0 \longrightarrow \frac{\omega_c}{\omega_h} \leqslant \frac{T_c}{T_h}. \tag{2.14}$$

We can obtain this results using the efficiency and the coefficient of performance (COP) defined in terms of the Bohr frequencies and using the Carnot upper bound.

$$\eta = \frac{P}{J_h} = 1 - \frac{\omega_c}{\omega_h} \leqslant \eta_C = 1 - \frac{T_c}{T_h} \tag{2.15}$$

$$\varepsilon = \frac{J_c}{P} = \frac{\omega_c}{\omega_h - \omega_c} \leqslant \varepsilon_C = \frac{T_c}{T_h - T_c}. \tag{2.16}$$

2.2.1   The system

This device can be studied in the context of open quantum systems, which will be studied in detail in chapter 3. To obtain the dynamics of our three level maser, we shall resort to the theory of periodically driven open quantum systems as described in [28–31].

In the weak coupling limit [17, 32], the stationary heat currents and power are given by:

$$\begin{aligned} J_c &= \omega_c I \\ J_h &= -\omega_h I \\ P &= -J_h - J_c = -(\omega_c - \omega_h)I \end{aligned} \tag{2.17}$$

where the flux I is given by

$$I = \frac{\Gamma_h \Gamma_c \left(e^{-\omega_c/T_c} - e^{-\omega_h/T_h}\right)}{\Gamma_h (1 + 2e^{-\omega_h/T_h}) + \Gamma_c (1 + 2e^{-\omega_c/T_c})}. \tag{2.18}$$

The relaxation rates for a bosonic bath can be take as $\Gamma_\alpha = \gamma_\alpha \omega_\alpha^{d_\alpha}[1 + N(\omega_\alpha)]$ with $\alpha = h, c$ [11, 19], with $N(\omega_\alpha) = (e^{\omega_\alpha/T_\alpha} - 1)^{-1}$ the occupation number for a Bose-Einstein distribution and d_α the physical dimension of the bosonic bath.

Using eqs. 2.13 and 2.14 we can define a maximum cold frequency as $\omega_{c,max} = \omega_h \frac{T_c}{T_h}$ for which the output power and cooling rate is zero.

For frequencies less than $\omega_{c,max}$ the system works as a refrigerator and has an optimal cooling rate at some frequency $\omega_c^R(\omega_h)$. On the other hand, for frequencies greater than $\omega_{c,max}$ the system works as thermal engine and has an optimal cooling rate at some frequency $\omega_c^E(\omega_h)$. Instead of using the cold frequency as a control parameter we are going to define the thermodynamic forces $x_c = \frac{\omega_c}{T_c}$ and $x_h = \frac{\omega_h}{T_h}$. In terms the thermodynamic forces equation 2.17 can be rewritten as

$$
\begin{aligned}
J_c &= \omega_c \frac{T_c}{T_c} I = T_c x_c I \\
J_c &= -\omega_h \frac{T_h}{T_h} I = -T_h x_h I \\
P &= -J_h - J_c = (T_h x_h - T_c x_c) I
\end{aligned}
\tag{2.19}
$$

and expressing the cold temperature T_c in terms of the Carnot efficiency and the COP as

$$
\begin{aligned}
\eta_C &= 1 - \frac{T_c}{T_h} \longrightarrow T_c = (1 - \eta_C) T_h & (2.20) \\
\epsilon_C &= \frac{Tc}{T_h - T_c} \longrightarrow T_c = \epsilon_C T_h - \epsilon_C T_c \longrightarrow T_c = \frac{T_h \epsilon_C}{1 + \epsilon_C} & (2.21)
\end{aligned}
$$

we can rewrite the cooling rate and power using this equations

$$
\begin{aligned}
J_c &= \frac{T_h \epsilon_C}{1 + \epsilon_C} x_c I & (2.22) \\
P &= T_h(x_h - (1 - \eta_C) x_c) I. & (2.23)
\end{aligned}
$$

To obtain the entropy production of the system we start from the second law of thermodynamics

$$
dS = \sum_{\alpha=h,c} \frac{\delta Q_\alpha}{T_\alpha} + \sigma
\tag{2.24}
$$

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where σ is entropy due to irreversible processes and $\sigma \geqslant 0$. Now we derived respect to time and we obtain

$$\dot{S} = \sum_{\alpha=h,c} \frac{J_\alpha}{T_\alpha} + \dot{\sigma}. \tag{2.25}$$

We are considering endoreversible thermodynamics so, the thermal machines follow a internal closed cycle and the entropy, being a state function, satisfies that $\dot{S} = 0$ from which we can obtain the entropy production as

$$\dot{\sigma} = - \sum_{\alpha=h,c} \frac{J_\alpha}{T_\alpha} \longrightarrow \dot{\sigma} = -\frac{J_h}{T_h} - \frac{J_c}{T_c} = (x_h - x_c)I. \tag{2.26}$$

Using the defined thermodynamic forces and equations 2.20 and 2.21 we can redefine the expressions 2.15 and 2.16 for the efficiency and COP of both, engines and refrigeratos as

$$\eta = 1 - \frac{\omega_c}{\omega_h} = 1 - \frac{x_c T_c}{x_h T_h} = 1 - \frac{x_c(1-\eta_C)\cancel{T_h}}{x_h \cancel{T_h}} \rightarrow \eta = 1 - (1-\eta_C)\frac{x_c}{x_h} \tag{2.27}$$

$$\epsilon = \frac{\omega_c}{\omega_h - \omega_c} = \frac{x_c T_c}{x_h T_h - x_c T_c} = \frac{1}{\frac{x_h T_h}{x_c T_c} - 1} = \frac{1}{\frac{\cancel{T_h} x_h}{x_c \frac{\cancel{T_h}\epsilon_C}{1+\epsilon_C}} - 1} \rightarrow \epsilon = \frac{\epsilon_C}{(1+\epsilon_C)\frac{x_h}{x_c} - \epsilon_C}. \tag{2.28}$$

We note that for a thermal engine the power has to be $P < 0$. Using the definition of power in terms of the fluxes, it must be satisfy that for engines $I < 0$ which according to equation 2.13 implies that $x_c > x_h$. A similar reasoning and taking into account that $J_c > 0$, it must be satisfied for refrigerators that $I > 0$ and according to equation 2.14 $x_c < x_h$. In the case which $x_c = x_h$ the flux I is zero. This operations region are shown in Figure 2.3.

Using this conditions, we see the that the second law of thermodynamics is never violated because always the condition $\dot{\sigma} \geqslant 0$ is fulfill.

2.2.2 Optimal Cooling Rate and Power Output

In this section we are going to introduce the optimization of the problem related to the efficiency at maximun cooling rate in terms of the cold thermodynamic force x_c. Here we reproduce the study done in [17].
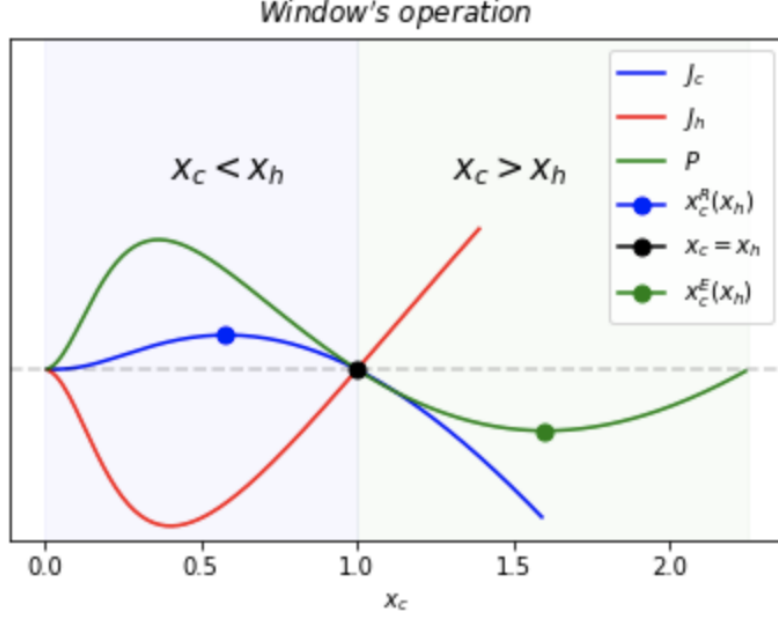
Figure 2.3: *Schematic depction of the heat currents and the window's operation of the device for $T_c = 4$, $T_h = 9$ (in arbitrary units),$\gamma_c = \gamma_h$ and $d_c = d_h = 3$. The optimal cold thermodynamic force for maximum cooling rate x_c^R and for maximum power output x_c^E are shown for fixed value f hot thermodynamic force $x_h = 1$. In the blue region the device operates as a refrigerator while in the green region behaves as an engine.*

Starting from equation 2.22 for the cooling rate, we obtain the optimal x_c for a refrigerator

$$(\frac{\partial J_c}{\partial x_c})_{x_c=x_c^R} = I + x_c(\frac{\partial I}{\partial x_c})_{x_c=x_c^R} = 0 \tag{2.29}$$

and for the output power in form of 2.23, we obtain the optimal x_c for a engine.

$$(\frac{\partial P}{\partial x_c})_{x_c=x_c^E} = -(1 - \eta_C)I + (x_h - (1 - \eta_C)x_c)(\frac{\partial I}{\partial x_c})_{x_c=x_c^E} = 0. \tag{2.30}$$

From both equations we obtain a solution $x_c^{(R,E)}(x_h)$, where R,E refer to a refrigerator and engines, respectively. These are transcendental equations, so the solution cannot be obtain analytically, but giving some numerical values we can obtain a graphic representation and see the form of this solutions in Fig. 2.4

The two function are monotonically increasing but we realize that in the case of refrigerators, for equals physical dimensionality of the baths $d_c = d_h = d$, the optimal cooling force
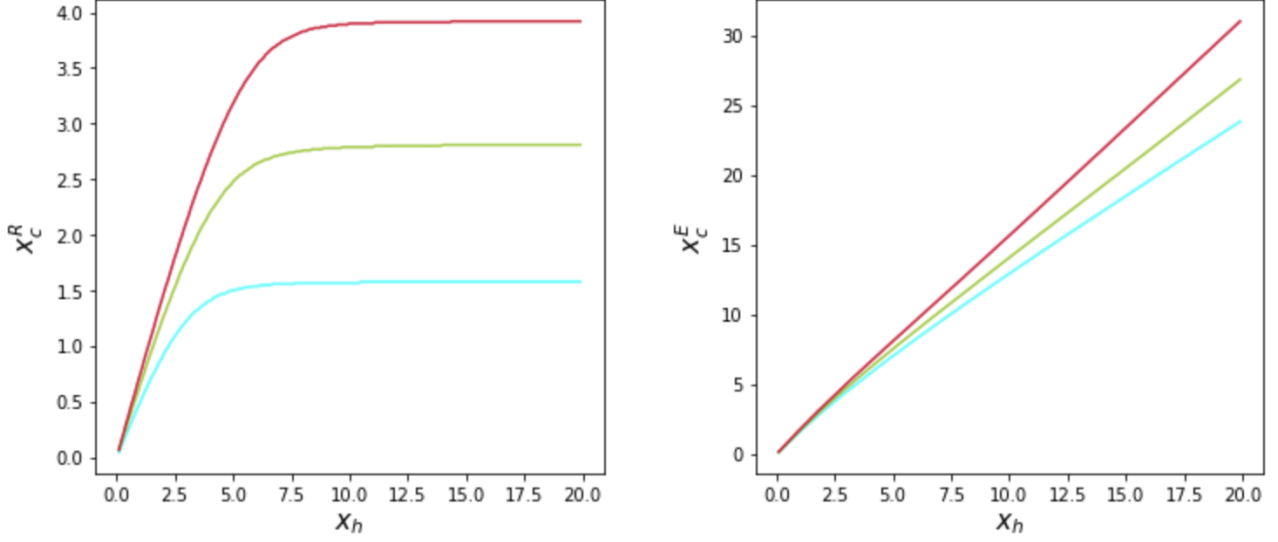
Figure 2.4: *Optimal cold thermodynamic force x_c^R and x_c^E as a function of hot force x_h for $T_c = 4$, $T_h = 9$ (in arbitrary units), $\gamma_c = \gamma_h$ and $d_c = d_h = 1$ (blue), 2(green), and 3 (red)*

saturates to a fixed value and we gonna prove this in detail. For large x_h the flux I (2.18) in terms of the thermodynamics forces is given by

$$I(x_h \longrightarrow \infty) = \frac{\gamma_c}{T_c^d} \frac{x_c^d}{1 - e^{x_c}}. \tag{2.31}$$

We introduce this expression in 2.29 and we obtain

$$\frac{T_c^{-d_h} \gamma_c (d_h x_c^{d_h}(-e^{x_c} + 1) + x_c^{d_h}(-e^{x_c} + 1) + x_c^{d_h+1} e^{x_c})}{(-e^{x_c} + 1)^2} = 0$$

$$(d+1)(1 - e^{x_c}) + x_c e^{x_c} = 0$$

$$d + 1 - (d+1)e^{x_c} + x_c e^{x_c} = 0 \longrightarrow (d + 1 - x_c)e^{x_c} = d + 1. \tag{2.32}$$

and doing the next change of variables $u = -(d + 1 - x_c)$

$$-u e^{d+1+u} = d + 1 \longrightarrow u e^u = -(d+1)e^{-(d+1)}.$$

This is the form of the Lambert function (https://www.wolframalpha.com/input/?i=lambert+w+function), so

$$u = W[-(d+1)e^{-(d+1)}].$$

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Undoing the change we obtain that the optimal x_c^R and cooling rate saturate to the fixed values

$$x_c^R(x_h \longrightarrow \infty) = d + 1 + W((-d-1)e^{-d-1})) \tag{2.33}$$

$$J_c^R((x_h \longrightarrow \infty)) = \frac{\gamma_c}{T_c^{d-1}} \frac{x_c^R(x_h \longrightarrow \infty)^{d+1}}{1 - e^{x_c^R(x_h \longrightarrow \infty)}}. \tag{2.34}$$

For example, in the case of $d = 3$ and $T_c = 4$ the optimal cooling force saturates to the value $x_c^R = 4$ (Fig. 2.4)

2.2.3 Performance in the regime of small forces

In this subsection, we are gonna to forget of our three level maser and develop a common model of endoreversible device with heat currents and power given by 2.19. We are going to study the machine in the case of small thermodynamic forces. To do that we expand the optimal value $x_c^{R,E}$ in power series of x_h

$$x_c^{(R,E)} = C_1^{(R,E)} x_h + C_2^{(R,E)} x_h^2 + \cdots. \tag{2.35}$$

For small x_h we can use a linear approximation such that $x_c^{(R,E)} \approx C_1^{(R,E)} x_h$. However we have to do different considerations for the coefficient $C_1^{(R,E)}$.

For refrigerators we obtain that $x_c < x_h$ (2.14) so the coefficient C_1^R, that will be a function of all the parameters of the problem, will satisfy

$$C_1^R(T_h, \epsilon_C, \Gamma_c, \Gamma_h, \cdots) \leqslant 1. \tag{2.36}$$

In terms of this coefficient we can rewrite the optimal COP, expression (2.28), at maximum cooling rate as

$$\epsilon^R = \frac{\epsilon_C}{(1 + \epsilon_C)\frac{1}{C_1^R} - \epsilon_C} = \frac{C_1^R \epsilon_C}{(1 - C_1^R)\epsilon_C + 1}. \tag{2.37}$$

For engines we obtain that $x_c > x_h$ (2.13) so the coefficient C_1^E that will be a function of all the parameters problem will satisfy

$$C_1^E(T_h, \epsilon_C, \Gamma_c, \Gamma_h, \cdots) \geqslant 1. \tag{2.38}$$

In terms of this coefficient we can rewrite the optimal efficiency expression (2.27) as

$$\eta^E = 1 - (1 - \eta_C)C_1^E. \qquad (2.39)$$

To obtain the coefficients $C_1^{(R,E)}$ we perform a Taylor expansion of the current I, with the form

$$I(x_c, x_h) = \sum_{i=c,h} I_i(0,0)x_i + \frac{1}{2!}\sum_{i,j=c,h} I_{ij}(0,0)x_i x_j + \frac{1}{3!}\sum_{i,j,k=c,h} I_{ijk}(0,0)x_i x_j x_k + \cdots . \qquad (2.40)$$

2.2.4 Linear term

For small thermodynamic forces we can assume that the first nonzero term in the Taylor expansion (2.40) is the linear term and because $I(x_h = x_c) = 0$ the current can be written as

$$I \approx I_0(x_h - x_c). \qquad (2.41)$$

Introducing this expression in equation 2.29 we can obtain the coefficient C_1^R because

$$I_0(x_h - x_c^R) - I_0 x_c^R = 0 \longrightarrow x_h - 2x_c^R = 0 \longrightarrow x_c^R = \frac{1}{2}x_h$$

so

$$C_1^R = \frac{1}{2}. \qquad (2.42)$$

On the other hand, introducing 2.41 in 2.30 we can obtain the coefficient C_1^E

$$
\begin{aligned}
-(1 - \eta_C)I_0(x_h - x_c^E) - I_0(x_h - (1 - \eta_C)x_c^E) &= 0 \\
2(1 - \eta_C)x_c^E - (2 - \eta_C)x_h &= 0 \\
x_c^E &= \frac{2 - \eta_c}{2(1 - \eta_C)}x_h \qquad (2.43)
\end{aligned}
$$

and therefore

$$C_1^E = \frac{2 - \eta_c}{2(1 - \eta_C)}. \qquad (2.44)$$

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Introducing this expressions of the coefficients in equations 2.37 and 2.39 we obtain the normalized COP, efficiency at maximum cooling rate and output power, respectively as

$$\epsilon^R = \frac{\frac{1}{2}\epsilon_C}{(1-\frac{1}{2})\epsilon_C + 1} \longrightarrow \frac{\epsilon^R}{\epsilon_C} = \frac{1}{2+\epsilon_C} \tag{2.45}$$

$$\eta^E = 1 - (1-\eta_C)\frac{2-\eta_c}{2(1-\eta_C)} \longrightarrow \frac{\eta^E}{\eta_C} = \frac{1}{2}. \tag{2.46}$$

With expression 2.46 we are showing the universality of efficiency in the case of linear response.

2.2.5 Higher orders

If the linear terms is zero, we have to go to higher orders in the expansion 2.40, assuming the particular form

$$I = I_0 x_c^{d-1}(x_h - x_c) \tag{2.47}$$

where d is model parameter. We can see that if $d = 1$ the linear case is recovered. Doing the same protocol as before we can obtain $C_1^{R,E}$.

Introducing 2.47 in equation 2.29 we can obtain the coefficient C_1^R

$$I_0 x_c^{R^{d-1}}(x_h - x_c^R) + x_c^R I_0[(d-1)x_c^{R^{d-2}}x_h - dx_c^{R^{d-1}}] = 0$$

$$I_0 x_c^{R^{d-1}}[(x_h - x_c^R + x_c^R((d-1)x_c^{R^{-1}}x_h - d)] = 0 \, dx_h - (1+d)x_c^R = 0$$

$$x_c^R = \frac{d}{d+1}x_h$$

so

$$C_1^R = \frac{d}{d+1}. \tag{2.48}$$

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Introducing [2.47](#) in equation [2.30](#) we can obtain the coefficient C_1^E

$$-(1 - \eta_C)I_0 x_c^{d-1}(x_h - x_c) + I_0 x_c^{d-2}[(d-1)x_h - dx_c][x_h - (1 - \eta_C)x_c] = 0$$

Taking out common factor of $I_0 x_c^{d-2}$

$$-(1-\eta_C)x_h x_c + (1-\eta_C)x_c^2 + (d-1)x_h^2 - d(1-\eta_C)x_h x_c + (1-\eta_C)x_h x_c - dx_h x_c + d(1-\eta_C)x_c^2 = 0$$

$$(1 - \eta_C)(d+1)(x_c^E)^2 + (\eta_C - 2)dx_h x_c^E + (d-1)x_h^2 = 0$$

Removing equal terms and regrouping terms we obtain the quadratic equation in the variable x_c^E

$$(1 - \eta_C)(d+1)(x_c^E)^2 + (\eta_C - 2)dx_h x_c^E + (d-1)x_h^2 = 0$$

$$x_c^E = \frac{-(\eta_C - 2)dx_h \pm \sqrt{(\eta_C - 2)^2 d^2 x_h^2 - 4(1 - \eta_C)(d+1)(d-1)x_h^2}}{2(1 - \eta_C)(d+1)}$$

$$x_c^E = \frac{(2 - \eta_C)d \pm \sqrt{d^2\eta_C^2 - \cancel{4\eta_C d^2} + \cancel{4d^2} - \cancel{4d^2} + 4 + \cancel{4\eta_C d^2} - 4\eta_C}}{2(1 - \eta_C)(d+1)} x_h$$
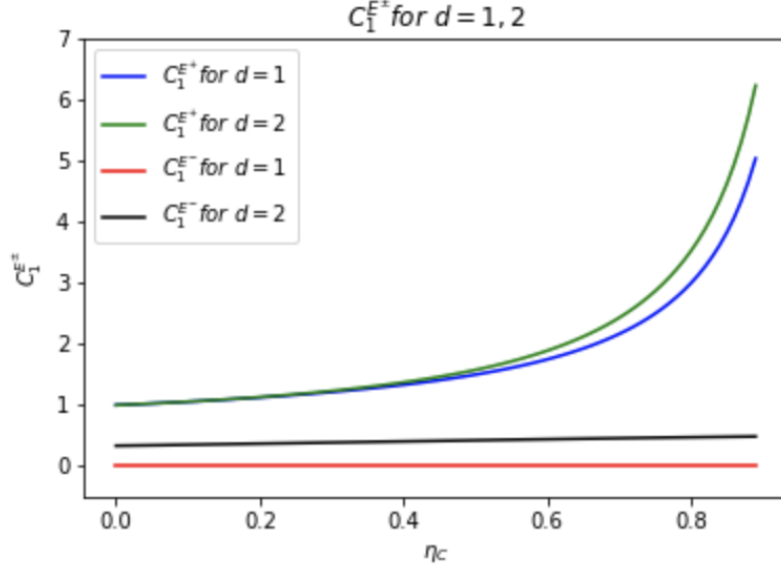
so we obtain two solutions for the coefficient C_1^E

$$C_1^{E\pm} = \frac{(2 - \eta_C)d \pm \sqrt{d^2\eta_C^2 - 4\eta_C + 4}}{2(1 - \eta_C)(d+1)}.$$

Only one solution is valid. To check the correct one we are going to plot both for $d = 1, 2$ (Fig. [2.5](#)) and see which of them satisfy the condition [2.38](#)

We can see that the one satisfy the condition [2.38](#) is

$$C_1^E = \frac{(2 - \eta_C)d + \sqrt{d^2\eta_C^2 - 4\eta_C + 4}}{2(1 - \eta_C)(d+1)}. \tag{2.49}$$

Figure 2.5: *Plot of the two solutions for the coefficients C_1^E. This figure shows that only the positive solution satisfy condition 2.28*

As before, introducing this coefficient in 2.37 and 2.39 we obtain the normalized COP, efficiency for maximum cooling rate and output power, respectively
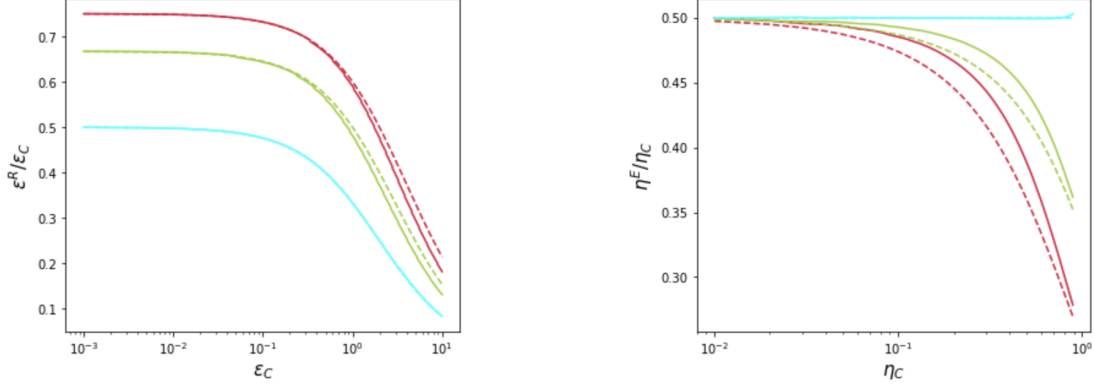
$$\epsilon^R = \frac{\frac{d}{d+1}\epsilon_C}{(1-\frac{d}{d+1})\epsilon_C+1} \longrightarrow \frac{\epsilon^R}{\epsilon_C} = \frac{\frac{1}{d+1}d}{\frac{1}{d+1}[(d+1-d)\epsilon_C]+d+1} \longrightarrow \frac{\epsilon^R}{\epsilon_C} = \frac{d}{d+1+\epsilon_C} \quad (2.50)$$

$$\eta^E = 1 - (1-\eta_C)\frac{(2-\eta_C)d+\sqrt{d^2\eta_C^2-4\eta_C+4}}{2(1-\eta_C)(d+1)} \longrightarrow \frac{\eta^E}{\eta_C} = \frac{2+d\eta_C-\sqrt{d^2\eta_C^2-4\eta_C+4}}{2(d+1)\eta_C}. \quad (2.51)$$

We are going to check that always, in the limit of vanishing η_C, the optimal efficiency η^E saturates to the fixed value $\eta_C/2$, that is the linear term in the expansion of Curzon-Ahlborn efficiency η_{CA} (2.10)

$$\lim_{\eta_C\to 0}\frac{\eta^E}{\eta_C} = \frac{0}{0} = \lim_{\eta_C\to 0}\frac{(2+d\eta_C)^2-(d^2\eta_C^2-4\eta_C+4)}{2(d+1)\eta_C\left(2+d\eta_C+\sqrt{d^2\eta_C^2+4\eta_C+4}\right)}$$

$$\lim_{\eta_C\to 0}\frac{\eta^E}{\eta_C} = \lim_{\eta_C\to 0}\frac{2}{\left(2+d\eta_C+\sqrt{d^2\eta_C^2+4\eta_C+4}\right)} = \frac{1}{2}. \quad (2.52)$$

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Figure 2.6: *Normalized optimal performance (solid line) for three level maser as a refrigerator (left) and as engine (right) vs the results of 2.50 and 2.51 (dashed-line). The parameters used are $x_h = 0.2$, $T_h = 9$ (in arbitrary units),$\gamma_c = \gamma_h$ and $d_c = d_h = d = 1$ (blue), 2(green), and 3 (red)*

So we can see that for any order in the limit of vanishing carnot efficiency $\eta^E \longrightarrow \eta_C/2$. This interesting result does not occur for COP. We can see in the next equation that the normalized COP saturates at different values for higher order.

$$\lim_{\epsilon_C \to 0} \frac{\epsilon^R}{\epsilon_C} = \frac{d}{d+1}. \tag{2.53}$$

This results are shown graphically in the next picture (2.6) and we can see also, that they are good approximation for the normalized efficiencies of our thermal machine.

2.2.6   Example: The Three-Level Maser in the Regime of High Temperatures

Now we go back to our system of interest: the three level maser. In terms of the thermodynamic forces the flux I (2.18) is given by

$$I = \frac{\Gamma_h \Gamma_c (e^{-x_c} - e^{-x_h})}{\Gamma_h (1 + 2e^{-x_h}) + \Gamma_c (1 + 2e^{-x_c})}. \tag{2.54}$$

We are going to study what happens with this flux in the regime of high temperatures, i.e, $x_c, x_h \ll 1$. We know that for $x \ll 1$ $e^{-x} \approx 1 - x$ and $e^x \approx 1 + x$, so considering this, we can rewrite the flux I

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$$I \approx \frac{\Gamma_h \Gamma_c (1 - x_c - 1 + x_h)}{\Gamma_h (3 - 2x_h) + \Gamma_c (3 - 2x_c)}.$$

and for $x \ll 1$,

$$I \approx \frac{\Gamma_h \Gamma_c (x_h - x_c)}{3(\Gamma_h + \Gamma_c)} \longrightarrow I \approx \frac{\Gamma_c (x_h - x_c)}{3(1 + \frac{\Gamma_c}{\Gamma_h})}, \tag{2.55}$$

where the rates Γ_α in terms of the thermodynamic forces are given by

$$\Gamma_\alpha = \gamma_\alpha x_\alpha^{d_\alpha} T_\alpha^{d_\alpha} \left(\frac{e^{x_\alpha}}{e^{x_\alpha} - 1} \right). \tag{2.56}$$

If we do a Taylor expansion of the last factor using

$$\frac{e^{x_\alpha}}{e^{x_\alpha} - 1} = \frac{1}{1 - e^{-x_\alpha}} = \frac{1}{x_\alpha} + \frac{1}{2} + \cdots + O(x_\alpha^6)$$

it follows that

$$\Gamma_\alpha = \gamma_\alpha x_\alpha^{d_\alpha - 1} T_\alpha^{d_\alpha}.$$

The quotient between the rates for the cold and hot bath results to be

$$\frac{\Gamma_c}{\Gamma_h} = \frac{\gamma_c x_c^{d_c - 1} T_c^{d_c}}{\gamma_h x_h^{d_h - 1} T_h^{d_h}} \tag{2.57}$$

and using eq. 2.21, eq. 2.57 can be written as

$$\frac{\Gamma_c}{\Gamma_h} = \frac{\gamma_c x_c^{d_c - 1}}{\gamma_h x_h^{d_h - 1}} T_h^{d_c - d_h} \left(\frac{\epsilon_C}{1 + \epsilon_C} \right)^{d_c}. \tag{2.58}$$

We can neglect this quotient in three ways: (a) in the limit of vanishing Carnot COP, $\epsilon_C \ll 1$, (b)$d_h = d_c = 1$ or (c)$\gamma_h \gg \gamma_h$. Whichever, eq.2.54 can be written as

$$I \propto x_c^{d_c - 1}(x_h - x_c) \tag{2.59}$$

which corresponds to eq. 2.47 and hence, to the results 2.50 and 2.51

Chapter 3

Open quantum systems

In general quantum systems are not isolated but are associated with an environment. We say in that way that quantum systems are open. An example of this are the atoms that are coupled to an electromagnetic field (EM). The EM causes spontaneous emission and absorption of photons.
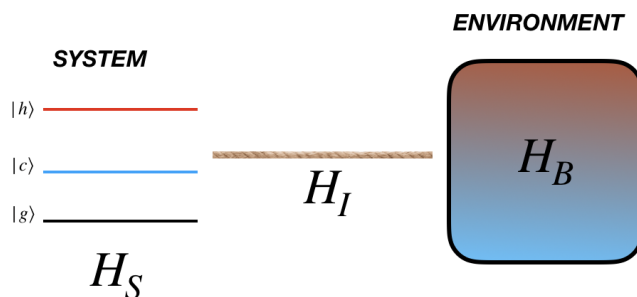
Figure 3.1: *Schematic picture of an open quantum system*

We consider a system S coupled to an external environment B and the interaction between them (Figure 3.1), The dynamics of the whole systems is described in a composite Hilbert space, i.e, $H_S \otimes H_B$. The Hamiltonian of our open quantum system is

$$H_T = H_S + H_B + H_I. \tag{3.1}$$

The dynamics of the total system is described by the Schrödinger equation (3.3). However,

as usually in this kind of systems, we are interested only in the properties and dynamics of the system **S**. These are described by the reduced density matrix $\rho_s(t)$, which we obtain applying the trace over the baths degrees of freedom on the total density matrix of the entire system $\rho(t)$, therefore

$$\rho_s = Tr_B\rho. \tag{3.2}$$

We are going to study in this chapter the dynamics of the reduce system. To do that we are going to make several approximations and considerations that will lead us to a so called *master equation* of the system. To make the derivation, we will follow the reference par excellence of theory of open quantum systems [11]. Later, in next chapter, we are going to apply this master equation to a particular case.

3.1   Review: Closed quantum systems

The time-development of the quantum state $|\psi(t)\rangle$ of a system with Hamiltonian $H(t)$ is ,using natural units $(\hbar = 1)$ governed by the well known Schrödinger equation

$$i\frac{d}{dt}|\psi(t)\rangle = H(t)|\psi(t)\rangle. \tag{3.3}$$

So we have a linear system and its evolution is completely determined by the initial state $|\psi(0)\rangle$. In this way, at time t the state of the system is characterized by

$$|\psi(t)\rangle = U(t, t_0)|\psi(0)\rangle \tag{3.4}$$

where $U(t, t_0)$ is the unitary evolution operator or also called quantum propagator. Introducing this expression in 3.3 and deriving, we obtain that the general form of this operator is

$$U(t, t_0) = \mathcal{T}\exp\left[-i\int_{t_o}^{t}H(\tau)\right], \tag{3.5}$$

with $\mathcal{T}$ the time order operator. If the system is in a mixed state $\rho(t)$, the evolution of the density matrix is completely determined by the initial density matrix $\rho(t_0)$, according to

$$\rho(t) = U(t, t_0)\rho(t_0)U^{\dagger}(t, t_0). \tag{3.6}$$

The evolution of $\rho(t)$ is ruled by the Liouville von Neumann equation:

$$\frac{d\rho(t)}{dt} = \mathcal{L}(t)\rho(t) \tag{3.7}$$

where the $\mathcal{L}$ is the Liouville operator and $\mathcal{L}(t)\rho(t) = -i\big[H(t), \rho(t)\big]$.

In the Heisenberg picture the states does not depend on time but operators do. So we have the unitary operator to characterize how the operators evolves in time. In this picture, we use the index H for operator, in such manner that

$$A_H(t) = U^\dagger(t, t_0)A(t)U(t, t_0), \tag{3.8}$$

and its evolution is determined by the next equation

$$i\frac{dA_H(t)}{dt} = [H_H, A_H(t)] + \frac{\partial A_H(t)}{\partial t}. \tag{3.9}$$

There exist a hybrid picture between the Schrörinder and Heisenberg picture. This representation is very useful for the cases where the hamiltonian has the following form

$$H(t) = H_0 + V(t) \quad ; \quad H_0 = H_S + H_B \tag{3.10}$$

where H_0 can be, also, a function of time and $V(t)$ describes the interaction between the two systems, in our case, between the system and the bath.

The operators evolves through $U_0(t, t_0)$ according to

$$A_I(t) = U_0^\dagger(t, t_0)A(t)U_0(t, t_0). \tag{3.11}$$

The hamiltonian that governs the evolution of the system in this picture is $V_I(t)$ and is defined by

$$V_I(t) = U_0^\dagger(t, t_0)V(t)U_0(t, t_0). \tag{3.12}$$

Also, the evolution operator in the interaction picture is $U_I(t, t_0) = U_0(t, t_0)U(t, t_0)$

The Von Neumann equation in this representation is given by

$$\frac{d}{dt}\rho_I(t) = -i[V_I(t), \rho_I(t)]. \tag{3.13}$$

In integral form we have

$$\rho_I(t) = \rho_I(t_0) - i \int_{t_0}^{t} d\tau [V_I(\tau), \rho_I(\tau)]. \tag{3.14}$$

3.2 Dynamical semigroups

Once we have reviewed how the dynamics of closed quantum system works, we move to our object of interest, open quantum systems.

Using equation 3.2 and 3.6 we can write for the density matrix of the system

$$\rho_s(t) = Tr_B\{U(t, t_0)\rho_S(t_0) \otimes \rho_B(t_0)U^\dagger(t, t_0)\}. \tag{3.15}$$

Where we have assumed the fact that the initial state of the entire system is in an uncorrelated state, i.e, $\rho(t_0) = \rho_S(t_0) \otimes \rho_B(t_0)$. While the evolution of a closed quantum system is described by an unitary operator (3.4), using the previous condition and for fixed t and given ρ_B, for example, a thermal state of the environment, one can described the evolution of the reduced system as the application of a dynamical map [11] over the initial state. Therefore,

$$\rho_s(t) = \Phi(t, t_0)\rho_s(t_0). \tag{3.16}$$

This assumption that we have done, in general, is not always true, and for initially correlated states several relevant consequences appear [33, 34].

We can obtain formally two exact equations of the reduced system's dynamics, one is eq. 3.16 and the second one, by taking partial trace over the Liouville von Neumman equation (3.7), accordingly

$$\frac{d\rho_S(t)}{dt} = -iTr_B[H(t), \rho(t)]. \tag{3.17}$$

However, we don't know the form of the dynamical map, so the problem is still unsolved. It is possible to obtain a more explicit form of the dynamical semigroup in the so called weak

coupling regime between the system and the environment (see figure 3.2). In this regime the enviroment recovers fast from the interaction with the system which evolves slowly. This condition allow us to neglect memory effects and to treat the evolution of the reduced system as Markovian [11, 33]. So, under this approximation, the dynamical map has the form of a contractive dynamical semigruoup [35]. Mathematically, the dynamical map satisfies the semigroup property

$$\Phi(t+s) = \Phi(t)\Phi(s) \ \ ; \ t,s \geqslant 0. \tag{3.18}$$

Let us mention, that this property allows us to give meaning to irreversible dynamics in a large class of of systems [11].

3.3 Microscopic derivation of Markovian Master Equation

Under a few conditions [11] it is possible to write the quantum dynamical semigroup in exponential form

$$\Phi(t) = e^{\mathcal{L}t}. \tag{3.19}$$

where $\mathcal{L}$ is a linear map that acts as the generator of the semigroup. This equation leads, using eq. 3.16, to the Markovian quantum master equation:

$$\frac{d}{dt}\rho_s(t) = \mathcal{L}\rho_s(t). \tag{3.20}$$

In this section we are going to obtain the superoperator $\mathcal{L}$ in the Gorini-Kossakowski-Lindblad-Sudarshan (GKLS) form [12, 13].

To do that we are going to perform a detailed derivation from a microscopic model [11], in the case that exist weak coupling between the system and the thermal baths (3.1).

We start by working in the interaction picture and omitting the index I for the density matrix, we can obtain the following evolution equation inserting 3.14 in 3.13 and assuming
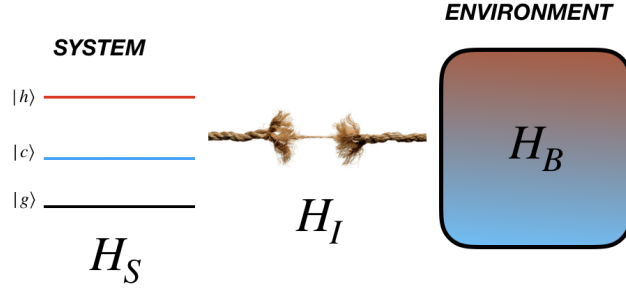
Figure 3.2: *Schematic picture of an open quantum system in the weak coupling limit*

that $t_0 = 0$

$$\frac{d}{dt}\rho(t) = -i[V_I(t), \rho(0)] - \int_0^t d\tau [V_I(t), [V_I(\tau), \rho(\tau)]]. \tag{3.21}$$

To obtain the reduce density $\rho_s(t)$, we have to apply the partial trace over the bath's degrees of freedom in the previous equation

$$\frac{d}{dt}\rho_s(t) = -iTr_B[V_I(t), \rho(0)] - \int_0^t d\tau Tr_B[V_I(t), [V_I(\tau), \rho(\tau)]]. \tag{3.22}$$

We have to assume that

$$Tr_B[V_I(t), \rho(0)] = 0. \tag{3.23}$$

Later we will underline that. So

$$\frac{d}{dt}\rho_s(t) = -\int_0^t d\tau Tr_B[V_I(t), [V_I(\tau), \rho(\tau)]]. \tag{3.24}$$

We have not yet perform any approximation, so this equation contains the same information than eq. 3.17.

The objective is to eliminate $\rho(t)$ in the previous equation. To achieve that, we apply the Born aproximation or weak coupling approximation that consist in assume that at time t the states of the system S and the bath B are still uncorrelated due to the fact that the environment recovers faster from the interaction while the system evolves slowly. Whereby,

$$\rho(t) \approx \rho_S(t) \otimes \rho_B. \tag{3.25}$$

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Hence, inserting this tensor product in equation in eq. 3.24, we obtain

$$\frac{d}{dt}p_s(t) = -\int_0^t d\tau Tr_B[V_I(t), [V_I(\tau), \rho_s(\tau) \otimes \rho_B]]. \tag{3.26}$$

We have to do more approximations to obtain the quantum master equation. First we realise that the evolution of the system is not local in time, but depends on its past value due to the integration over $\rho_s(\tau)$. So we have to do a Markov approximation and replace $\rho_S(\tau)$ by $\rho_S(t)$ makin eq. 3.26 time-local.

$$\frac{d}{dt}\rho_s(t) = -\int_0^t d\tau Tr_B[V_I(t), [V_I(\tau), \rho_s(t) \otimes \rho_B]]. \tag{3.27}$$

The last expression is known as Redlfield equation. This equation is local in time but is not Markovian because still depends on the initial condition $\rho(0)$. To obtain a fully Markovian evolution we have to do what is known as Born-Markov approximation.

This consists in replacing $\tau \longrightarrow t - \tau$ considering that the bath's time correlation, τ_B is smaller than the relaxation time of the system τ_R and the internal dynamics time τ. In other words, $\tau_B \ll \tau_R$ and $\tau_B \ll \tau$. So, this allow us to establish the upper limit in $t = \infty$ and obtain the Markovian quantum master equation:

$$\frac{d}{dt}\rho_s(t) = -\int_0^\infty d\tau Tr_B[V_I(t), [V_I(t - \tau), \rho_s(t) \otimes \rho_B]]. \tag{3.28}$$

However, this equation not ensure the definition of the superoperator $\mathcal{L}$ of the dynamical semigroup in the GKLS form. To bring this result we have to do an approximation known as secular approximation or rotating wave approximation (RWA). Before that, we have to give some definitions.

In the Schrödinger picture, generally, the interaction hamiltonian between the system and the bath has the following form

$$H_I = \sum_\alpha S_\alpha \otimes B_\alpha. \tag{3.29}$$

To continue with the derivation it should be convenient write the fourier representation of de system operators $S(t)$, and for this is necessary suppose that H_S has a discret spectrum.

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Defining H_S in his spectral values, and taking into account that ϵ are his eigenvalues and $\Pi(\epsilon)$ the projections in the eigenspace associated to the eigenvalue ϵ

$$H_S = \sum_\epsilon \epsilon \, |\epsilon\rangle \, \langle\epsilon| . \tag{3.30}$$

Thereby, with the condition that the energy differences of two states $\epsilon - \epsilon'$ coincide with with the Bohr frequency of the system $(\epsilon - \epsilon' = \omega)$

$$S_\alpha(\omega) = \sum_{\epsilon\epsilon'} \Pi(\epsilon) S_\alpha \Pi(\epsilon') = \sum_{\epsilon\epsilon'} |\epsilon\rangle \, \langle\epsilon| \, S_\alpha \, |\epsilon'\rangle \, \langle\epsilon'| . \tag{3.31}$$

We can prove that $S_\alpha(\omega)$ and $S_\alpha^\dagger(\omega)$ are eigenoperators of H_S applying the following commutator

$$
\begin{aligned}
[H_S, S_\alpha(\omega)] &= \sum_{\epsilon''} \sum_{\epsilon\epsilon'} \epsilon'' \, |\epsilon''\rangle \, \langle\epsilon''|\epsilon\rangle \, S_{\alpha_{\epsilon\epsilon'}} \, \langle\epsilon'| - \sum_{\epsilon\epsilon'} \sum_{\epsilon''} \epsilon'' \, |\epsilon\rangle \, S_{\alpha_{\epsilon\epsilon'}} \, \langle\epsilon'|\epsilon''\rangle \, \langle\epsilon''| \\
&= \sum_{\epsilon''} \sum_{\epsilon\epsilon'} \epsilon'' \, |\epsilon''\rangle \, \delta_{\epsilon''\epsilon} S_{\alpha_{\epsilon\epsilon'}} \, \langle\epsilon'| - \sum_{\epsilon\epsilon'} \sum_{\epsilon''} \epsilon'' \, |\epsilon\rangle \, S_{\alpha_{\epsilon\epsilon'}} \delta_{\epsilon'\epsilon''} \, \langle\epsilon''| \\
&= \sum_{\epsilon\epsilon'} \epsilon \, |\epsilon\rangle \, S_{\alpha_{\epsilon\epsilon'}} \, \langle\epsilon'| - \sum_{\epsilon\epsilon'} \epsilon' \, |\epsilon\rangle \, S_{\alpha_{\epsilon\epsilon'\epsilon'}} \, \langle\epsilon''| = (\epsilon - \epsilon') S_\alpha(\omega). \tag{3.32}
\end{aligned}
$$

Applying the same procedure for $S_\alpha^\dagger(\omega)$ we have the following expressions

$$[H_S, S_\alpha(\omega)] = -\omega S_\alpha(\omega) \qquad [H_S, S_\alpha^\dagger(\omega)] = +\omega S_\alpha^\dagger(\omega) \tag{3.33}$$

with the condition

$$S_\alpha^\dagger(\omega) = S_\alpha(-\omega). \tag{3.34}$$

Defining the corresponding operators in the interaction picture using equation 3.11 and taking into account that H_B only acts on the enviroment's Hilbert space, we can sum over all possible energy differences and obtain the wanted representation of the system operator S

$$
\begin{aligned}
S(t) &= \sum_\omega U_S(t) S_\alpha(\omega) U_S^\dagger(t) = \sum_\omega e^{iH_S t} S_\alpha(\omega) e^{-iH_S t} = \sum_\omega \sum_{\epsilon\epsilon'} e^{iH_S t} \, |\epsilon\rangle \, S_{\alpha_{\epsilon\epsilon'}} \, \langle\epsilon'| \, e^{-iH_S t} \\
&= \sum_\omega \sum_{\epsilon\epsilon'} e^{i\epsilon t} \, |\epsilon\rangle \, S_{\alpha_{\epsilon\epsilon'}} \, \langle\epsilon'| \, e^{-i\epsilon' t} \longrightarrow S_\alpha(t) = \sum_\omega S_\alpha(\omega) e^{-i\omega t}. \tag{3.35}
\end{aligned}
$$

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The fact that having introduced this spectral form allow us to define the interaction hamiltonian in the interaction picture (3.12) as

$$V_I(t) = \sum_\alpha S_\alpha(t)B_\alpha(t) = \sum_{\omega,\alpha} S_\alpha(\omega)B_\alpha(t)e^{-i\omega t} = \sum_{\omega,\alpha} S_\alpha^\dagger(\omega)B_\alpha^\dagger(t)^\dagger e^{i\omega t} \qquad (3.36)$$

where $B_\alpha(t) = e^{iH_B t}B_\alpha e^{iH_B t}$ are the bath operators en the interaction picture. This previous definition and the condition of ρ_B is a stationary state of H_B proves the assumption 3.23 because

$$\langle B_\alpha(t)\rangle = 0. \qquad (3.37)$$

Going back to the evolution equation of the reduced system (3.28), we develope the commutator of the integrand as

$$
\begin{aligned}
\Big[V_I(t), [V_I(t-\tau), \rho_s(t)\otimes\rho_B]\Big] &= [V_I(t), (V_I(t-\tau)\rho_s(t)\rho_B - \rho_s(t)\rho_B V_I(t-\tau))] \\
&= V_I(t)V_I(t-\tau)\rho_s(t)\rho_B - V_I(t-\tau)\rho_s(t)\rho_B V_I(t) - V_I(t)\rho_s(t)\rho_B V_I(t-\tau)) + \rho_s(t)\rho_B V_I(t-\tau)V_I(t) \\
&= -[V_I(t-\tau)\rho_s(t)\rho_B V_I(t) - V_I(t)V_I(t-\tau)\rho_s(t)\rho_B] + h.c.
\end{aligned}
\qquad (3.38)
$$

Introducing this expression in 3.28 we obtain

$$\frac{d}{dt}\rho_s(t) = \int_0^\infty d\tau\, Tr_B\{V_I(t-\tau)\rho_s(t)\rho_B V_I(t) - V_I(t)V_I(t-\tau)\rho_s(t)\rho_B\} + h.c. \qquad (3.39)$$

Then if we introduce the form 3.36 of V_I and taking into account the lineal property of the trace $\Big(Tr(A+B) = TrA + TrB\Big)$

$$\frac{d}{dt}\rho_s(t) = \int_0^\infty d\tau Tr_B\{V_I(t-\tau)\rho_s(t)\rho_B V_I(t)\} - \int_0^\infty d\tau tr_B\{V_I(t)V_I(t-\tau)\rho_s(t)\rho_B\} + h.c$$

$$\frac{d}{dt}\rho_s(t) = \int_0^\infty d\tau Tr_B\{\sum_{\omega,\beta} S_\beta(\omega)B_\beta(t-\tau)e^{-i\omega(t-\tau)}\rho_s(t)\rho_B \sum_{\omega',\alpha} S_\alpha^\dagger(\omega')B_\alpha^\dagger(t)^\dagger e^{i\omega' t}\}$$

$$- \int_0^\infty d\tau Tr_B\{\sum_{\omega',\alpha} S_\alpha^\dagger(\omega')B_\alpha^\dagger(t)^\dagger e^{i\omega' t} \sum_{\omega,\beta} S_\beta(\omega)B_\beta(t-\tau)e^{-i\omega(t-\tau)}\rho_s(t)\rho_B\} + h.c$$

$$\frac{d}{dt}\rho_s(t) = \int_0^\infty d\tau \sum_{\omega,\omega'}\sum_{\alpha,\beta} e^{i(\omega-\omega')t} S_\beta(\omega)\rho_s(t)S_\alpha^\dagger(\omega')e^{i\omega\tau} Tr_B\{B_\beta(t-\tau)\rho_B B_\alpha^\dagger(t)\}$$

$$- \int_0^\infty d\tau \sum_{\omega,\omega'}\sum_{\alpha,\beta} e^{i(\omega-\omega')t} S_\alpha^\dagger(\omega')S_\beta(\omega)\rho_s(t)e^{i\omega\tau} tr_B\{B_\alpha^\dagger(t)B_\beta(t-\tau)\rho_B\} + h.c. \qquad (3.40)$$

The trace has a cycle property $\left(TrABC = TrCAB\right)$ and due to the definition of the mean value of an operator for a mixed state we can define the bath or reservoir correlation functions

$$Tr_B\{B_\alpha^\dagger(t)B_\beta(t-\tau)\rho_B\} = \langle B_\alpha^\dagger(t)B_\beta(t-\tau)\rangle. \qquad (3.41)$$

So in this case, we have that

$$\frac{d}{dt}\rho_s(t) = \sum_{\omega,\omega'}\sum_{\alpha\beta} e^{i(\omega-\omega')t}\mathcal{C}_{\alpha\beta}(\omega,t)\left(S_\beta(\omega)\rho_s(t)S_\alpha^\dagger(\omega') - S_\alpha^\dagger(\omega')S_\beta(\omega)\rho_s(t)\right) + h.c \qquad (3.42)$$

where $\sigma_{\alpha\beta}(\omega,t)$ is the one side Fourier-transform

$$\mathcal{C}_{\alpha\beta}(\omega,t) = \int_0^\infty d\tau e^{i\omega\tau}\langle B_\alpha^\dagger(t)B_\beta(t-\tau)\rangle. \qquad (3.43)$$

In principle, this function depends on time but with the supposition that ρ_B is a stationary state of H_B, it can be proved ([36]) that the reservoir correlation functions are homogeneous in time, thus it, only depends on the time differences. In this way, the one side Fourier-transform becomes time-independent

$$\mathcal{C}_{\alpha\beta}(\omega) = \int_0^\infty d\tau e^{i\omega\tau}\langle B_\alpha^\dagger(\tau)B_\beta(0)\rangle. \qquad (3.44)$$

Now, we have to do a secular approximation or rotating wave approximation. Defining the evolution time of the system τ_S like $1/|\omega - \omega'|$ and assuming that this time is much larger than the relaxation time τ_R of the system, the terms with $\omega \neq \omega'$ are going to oscillate to fast respect τ_S,so, it can be neglected. In this way,

$$\frac{d}{dt}\rho_s(t) = \sum_{\omega}\sum_{\alpha,\beta}\mathcal{C}_{\alpha\beta}(\omega)\left(S_\beta(\omega)\rho_s(t)S_\alpha^\dagger(\omega) - S_\alpha^\dagger(\omega)S_\beta(\omega)\rho_s(t)\right) + h.c \qquad (3.45)$$

and including the hermitian conjugate we obtain

$$
\begin{aligned}
\frac{d}{dt}\rho_s(t) &= \sum_\omega \sum_{\alpha,\beta} \mathcal{C}_{\alpha\beta}(\omega)\Big(S_\beta(\omega)\rho_s(t)S_\alpha^\dagger(\omega) - S_\alpha^\dagger(\omega)S_\beta(\omega)\rho_s(t) \Big) \\
&+ \sum_\omega \sum_{\alpha,\beta} \mathcal{C}_{\alpha\beta}^*(\omega)\Big(S_\alpha(\omega)\rho_s(t)S_\beta^\dagger(\omega) - \rho_s(t)S_\beta^\dagger(\omega)S_\alpha(\omega) \Big).
\end{aligned}
\tag{3.46}
$$

Defining $\mathcal{C}_{\alpha\beta}(\omega)$ [36] in a real and imaginary part

$$
\mathcal{C}_{\alpha\beta}(\omega) = \frac{1}{2}\Gamma_{\alpha\beta}(\omega) + i\nu_{\alpha\beta}(\omega)
\tag{3.47}
$$

where

$$
\Gamma_{\alpha\beta}(\omega) = \mathcal{C}_{\alpha\beta}(\omega) + \mathcal{C}_{\alpha\beta}^*(\omega) \quad \nu_{\alpha\beta}(\omega) = \frac{1}{2i}(\mathcal{C}_{\alpha\beta}(\omega) - \mathcal{C}_{\alpha\beta}^*(\omega))
\tag{3.48}
$$

we have for eq. 3.46

$$
\begin{aligned}
\frac{d}{dt}\rho_s(t) &= \sum_\omega \sum_{\alpha,\beta} \mathcal{C}_{\alpha\beta}(\omega)S_\beta(\omega)\rho_s(t)S_\alpha^\dagger(\omega) + \sum_\omega \sum_{\alpha,\beta} \mathcal{C}_{\alpha\beta}^*(\omega)S_\alpha(\omega)\rho_s(t)S_\beta^\dagger(\omega) \\
&- \sum_\omega \sum_{\alpha,\beta} \mathcal{C}_{\alpha\beta}(\omega)S_\alpha^\dagger(\omega)S_\beta(\omega)\rho_s(t) - \sum_\omega \sum_{\alpha,\beta} \mathcal{C}_{\alpha\beta}^*(\omega)\rho_s(t)S_\beta^\dagger(\omega)S_\alpha(\omega)).
\end{aligned}
\tag{3.49}
$$

If we interchange the indexes α,β in the second and last summands

$$
\begin{aligned}
\frac{d}{dt}\rho_s(t) &= \sum_\omega \sum_{\alpha,\beta} \mathcal{C}_{\alpha\beta}(\omega)S_\beta(\omega)\rho_s(t)S_\alpha^\dagger(\omega) + \sum_\omega \sum_{\alpha,\beta} \mathcal{C}_{\beta\alpha}^*(\omega)S_\beta(\omega)\rho_s(t)S_\alpha^\dagger(\omega) \\
&- \sum_\omega \sum_{\alpha,\beta} \mathcal{C}_{\alpha\beta}(\omega)S_\alpha^\dagger(\omega)S_\beta(\omega)\rho_s(t) - \sum_\omega \sum_{\alpha,\beta} \mathcal{C}_{\beta\alpha}^*(\omega)\rho_s(t)S_\alpha^\dagger(\omega)S_\beta(\omega)).
\end{aligned}
\tag{3.50}
$$

Now we use the definitions 3.47 and 3.48

$$
\begin{aligned}
\frac{d}{dt}\rho_s(t) &= \sum_\omega \sum_{\alpha,\beta} \Big(\mathcal{C}_{\alpha\beta}(\omega) + \mathcal{C}_{\beta\alpha}^*(\omega) \Big)S_\beta(\omega)\rho_s(t)S_\alpha^\dagger(\omega) \\
&- \sum_\omega \sum_{\alpha,\beta} \Big(\tfrac{1}{2}\Gamma_{\alpha\beta}(\omega) + i\nu_{\alpha\beta}(\omega) \Big)S_\alpha^\dagger(\omega)S_\beta(\omega)\rho_s(t) \\
&- \sum_\omega \sum_{\alpha,\beta} \Big(\tfrac{1}{2}\Gamma_{\beta\alpha}^*(\omega) + i\nu_{\beta\alpha}^*(\omega) \Big)\rho_s(t)S_\alpha^\dagger(\omega)S_\beta(\omega)).
\end{aligned}
\tag{3.51}
$$

It can be proved that $\Gamma_{\alpha\beta} = \Gamma^*_{\beta\alpha}$ and $\nu_{\alpha\beta} = \nu^*_{\beta\alpha}$ [36], so

$$
\begin{aligned}
\frac{d}{dt}\rho_s(t) &= \sum_\omega \sum_{\alpha,\beta} \Gamma_{\alpha\beta}(\omega) S_\beta(\omega) \rho_s(t) S^\dagger_\alpha(\omega) - \frac{1}{2}\sum_\omega \sum_{\alpha,\beta} \Gamma_{\alpha\beta}(\omega) S^\dagger_\alpha(\omega) S_\beta(\omega) \rho_s(t) \\
&\quad - \frac{1}{2}\sum_\omega \sum_{\alpha,\beta} \Gamma_{\alpha\beta}(\omega) \rho_s(t) S^\dagger_\alpha(\omega) S_\beta(\omega) - i\sum_\omega \sum_{\alpha,\beta} \nu_{\alpha\beta}(\omega) S^\dagger_\alpha(\omega) S_\beta(\omega) \rho_s(t) \\
&\quad + i\sum_\omega \sum_{\alpha,\beta} \nu_{\alpha\beta}(\omega) \rho_s(t) S^\dagger_\alpha(\omega) S_\beta(\omega).
\end{aligned}
\tag{3.52}
$$

Taking into account the definition of the anticommutator between two operator A and B ($\{A, B\} = AB + BA$), 3.52 can be written

$$
\begin{aligned}
\frac{d}{dt}\rho_s(t) &= \sum_\omega \sum_{\alpha,\beta} \Gamma_{\alpha\beta}(\omega) S_\beta(\omega) \rho_s(t) S^\dagger_\alpha(\omega) - \frac{1}{2}\sum_\omega \sum_{\alpha,\beta} \Gamma_{\alpha\beta}(\omega)\left\{ S^\dagger_\alpha(\omega) S_\beta(\omega), \rho_s(t) \right\} \\
&\quad - i\sum_\omega \sum_{\alpha,\beta} \nu_{\alpha\beta}(\omega) S^\dagger_\alpha(\omega) S_\beta(\omega) \rho_s(t) + i\sum_\omega \sum_{\alpha,\beta} \nu_{\alpha\beta}(\omega) \rho_s(t) S^\dagger_\alpha(\omega) S_\beta(\omega).
\end{aligned}
\tag{3.53}
$$

and defining $H_{LS} = \sum_\omega \sum_{\alpha,\beta} \nu_{\alpha\beta}(\omega) S^\dagger_\alpha(\omega) S_\beta(\omega)$, the master equation in interaction picture can be written as

$$
\frac{d}{dt}\rho_s(t) = -i\left[H_{LS}, \rho_s \right] + \sum_\omega \sum_{\alpha,\beta} \Gamma_{\alpha\beta}(\omega)\left(S_\beta(\omega)\rho_s(t)S^\dagger_\alpha(\omega) - \frac{1}{2}\left\{ S^\dagger_\alpha(\omega) S_\beta(\omega), \rho_s(t) \right\} \right).
\tag{3.54}
$$

The term associated to H_{LS} takes into account Lamb Shift which produces a correction (or splitting) in the energies of the system due to the coupling between system and environment. This term includes oscillation in the dynamics of the system.

This last equation is the master equation in the interaction picture. Its form in the Schöringer picture is obtained by adding the hamiltonian system H_S to H_{LS}, hence

$$
\frac{d}{dt}\rho_s(t) = -i\left[H_S + H_{LS}, \rho_s \right] + \mathcal{D}\big(\rho_s(t)\big) = \mathcal{L}\rho_s(t)
\tag{3.55}
$$

where $\mathcal{D}$ is the dissipator of the system and is defined by

$$
\mathcal{D}\big(\rho_s(t)\big) = \sum_\omega \sum_{\alpha,\beta} \Gamma_{\alpha\beta}(\omega)\left(S_\beta(\omega)\rho_s(t)S^\dagger_\alpha(\omega) - \frac{1}{2}\left\{ S^\dagger_\alpha(\omega) S_\beta(\omega), \rho_s(t) \right\} \right).
\tag{3.56}
$$

This is not the GKLS form of the master equation. To obtain it, we have to diagonalize eq. 3.55. The matrix $\Gamma_{\alpha\beta}$ is defined as [11]

$$\Gamma_{\alpha\beta}(\omega) = \int_{-\infty}^{\infty} d\tau e^{i\omega\tau} \langle B_\alpha^\dagger(\tau) B_\beta(0) \rangle. \qquad (3.57)$$

which is a positive quantity [11, 36]. This allow us to make a diagonalization and obtain the GKLS master equation

$$\frac{d}{dt}\rho_s(t) = -i\left[H_S + H_{LS}, \rho_s\right] + \sum_\omega \sum_\alpha \Gamma_\alpha(\omega)\left(S_\alpha(\omega)\rho_s(t)S_\alpha^\dagger(\omega) - \frac{1}{2}\left\{S_\alpha^\dagger(\omega)S_\alpha(\omega), \rho_s(t)\right\}\right). \; (3.58)$$

We will use in next chapter this equation to study a particular system, the quantum tricycle.

Chapter 4

The quantum tricycle

We have studied in chapter 2 the optimization of an open system that acts as a QTM: The three level maser. Once the theory of open system has been reviewed (ch.3), it seems logical to proceed with the derivation of the steady heat currents (2.17) and the flux I (2.18) of this system.

However, the resolution of the quantum master equation for the three level maser is not so simple because this system is periodically driven by an external field and another considerations has to be taken into account, in particular it is convenient to use the Floquet theory. We are not going to study this in depth, we refer the reader to [28–30] for a well structured and detailed discussion of the subject.

However, in order to bring an open quantum system which can be analyze with the theory expose in previous chapter, we are going to study a similar one to the Three level maser: The quantum tricycle [16].

4.1 The model

In the quantum tricycle (Fig. 4.1), the transition between the cold and hot levels that is periodically driven by an external field in the three level maser, is coupled by a frequency filter to another unstructured bosonic bath at temperature T_w ($T_w > T_h > T_c$) which acts

as the work bath. If $T_w \longrightarrow \infty$ no entropy is generated in the work bath, so the current J_w is pure power P. In such conditions one can think that we are gonna recover the results of the quantum amplifier but this is not true and we gonna prove that.
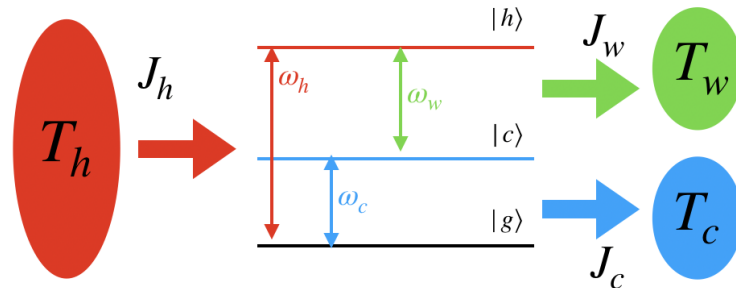
Figure 4.1: *The quantum tricycle as a QHE. If we reverse the cycle we obtain a quantum absorption refrigerator.*

The total system's Hamiltonian has the form of 3.1 and H_S, H_B and H_I are respectively:

$$H_S = \sum_{i=\{g,c,h\}} \epsilon_i \left| i \right\rangle \left\langle i \right| \tag{4.1}$$

$$H_B = \sum_{\alpha=\{w,c,h\}} \sum_{\lambda} \omega_\lambda b_{\alpha\lambda}^\dagger b_{\alpha\lambda} \tag{4.2}$$

$$H_I = \sum_{\alpha} S_\alpha \otimes B_\alpha \tag{4.3}$$

where the system operators are the following thermal contact operators [32]

$$S_h = \left| g \right\rangle \left\langle h \right| + \left| h \right\rangle \left\langle g \right| \quad S_c = \left| g \right\rangle \left\langle c \right| + \left| c \right\rangle \left\langle g \right| \quad S_w = \left| c \right\rangle \left\langle h \right| + \left| h \right\rangle \left\langle c \right| \tag{4.4}$$

and the reservoir operators B_α are [32]

$$B_\alpha = \sum_{\lambda} \sqrt{\gamma_\alpha \omega_\lambda} (b_{\alpha\lambda} + b_{\alpha\lambda}^\dagger) \tag{4.5}$$

with the condition that the constants $\sqrt{\gamma_\alpha \omega_\lambda}$ indicate the strength of the bath's mode with the transitions of the three level system to ensure flat spectral density $J(\omega)$ [11, 18, 32]

4.2 Markovian master equation

We have obtained in the previous chapter that the evolution of the system density operator of an open quantum system satisfy in the Schrödinger picture the next master equation

$$\frac{d}{dt}\rho_s(t) = -i\Big[H_S + H_{LS}, \rho_s\Big] + \sum_\omega \sum_\alpha \Gamma_\alpha(\omega)\Big(S_\alpha(\omega)\rho_s(t)S_\alpha^\dagger(\omega) - \frac{1}{2}\big\{S_\alpha^\dagger(\omega)S_\alpha(\omega), \rho_s(t)\big\}\Big). \quad (4.6)$$

If we neglect the Lamb Shift Hamiltonian as is usually in quantum optics because the oscillations that included in the system are too small, the markovian master equation becomes

$$\frac{d}{dt}\rho_s(t) = -i\Big[H_S, \rho_s\Big] + \sum_\omega \sum_\alpha \Gamma_\alpha(\omega)\Big(S_\alpha(\omega)\rho_s(t)S_\alpha^\dagger(\omega) - \frac{1}{2}\big\{S_\alpha^\dagger(\omega)S_\alpha(\omega), \rho_s(t)\big\}\Big) \quad (4.7)$$

where we remember that $\Gamma_\alpha(\omega)$ was the real part of the one side Fourier transform (eq. 3.57) and it can be prove [11] that for unstructured bosonic baths and flat spectral density this transition rate is

$$\Gamma_\alpha(\omega) = \gamma_\alpha \omega_\alpha^{d_\alpha}[1 + N(\omega_\alpha)]. \quad (4.8)$$

Considering the properties of out system the set of possibles frequencies are

$$\Lambda = \{\pm\omega_h, \pm\omega_c, \pm\omega_w = \pm(\omega_h - \omega_c)\} \quad (4.9)$$

so we can separate the sum of 4.7 in two terms taking positives frequencies

$$\begin{aligned}
\frac{d}{dt}\rho_s(t) &= -i\Big[H_S, \rho_s\Big] + \sum_{\omega>0\,\omega\varepsilon\Lambda}\sum_{\alpha=h,c,w}\Big\{\Gamma_\alpha(\omega)\Big(S_\alpha(\omega)\rho_s(t)S_\alpha^\dagger(\omega) - \frac{1}{2}\big\{S_\alpha^\dagger(\omega)S_\alpha(\omega), \rho_s(t)\big\}\Big) \\
&\quad + \Gamma_\alpha(-\omega)\Big(S_\alpha(-\omega)\rho_s(t)S_\alpha^\dagger(-\omega) - \frac{1}{2}\big\{S_\alpha^\dagger(-\omega)S_\alpha(-\omega), \rho_s(t)\big\}\Big)\Big\}. \quad (4.10)
\end{aligned}$$

This equation can be rewritten as

$$\frac{d}{dt}\rho_s(t) = -i\Big[H_S, \rho_s\Big] + \sum_{\alpha=h,c,w} \mathcal{D}_\alpha\big(\rho_s(t)\big) \tag{4.11}$$

where $\mathcal{D}_\alpha\big(\rho_s(t)\big)$ are the dissipators of each bath.

Using equation 3.31 and the condition 3.34 we can obtain the spectral form of the system operators (4.4). Hence

$$S_h(\omega) = |g\rangle\langle h| \quad S_h^\dagger(\omega) = |h\rangle\langle g|$$

$$S_c(\omega) = |g\rangle\langle c| \quad S_c^\dagger(\omega) = |c\rangle\langle g|$$

$$S_w(\omega) = |c\rangle\langle h| \quad S_w^\dagger(\omega) = |h\rangle\langle c|. \tag{4.12}$$

With these definitions and eq. 4.10 we can obtain the form of the bath dissipators starting with the dissipator of the hot bath.

$$\mathcal{D}_h(\rho_s) = \sum_{\omega>0} \Gamma_h(\omega)\Big(S_h(\omega)\rho_s S_h^\dagger(\omega) - \tfrac{1}{2}\big\{S_h^\dagger(\omega)S_h(\omega), \rho_s\big\}\Big)$$
$$+ \sum_{\omega>0} \Gamma_h(-\omega)\Big(S_h(-\omega)\rho_s S_h^\dagger(-\omega) - \tfrac{1}{2}\big\{S_h^\dagger(-\omega)S_h(-\omega), \rho_s\big\}\Big) \tag{4.13}$$

$$\mathcal{D}_h(\rho_s) = \sum_{\omega>0} \Gamma_h(\omega)\Big(|g\rangle\langle h| \rho_s |h\rangle\langle g| - \frac{1}{2}(|h\rangle\langle g|g\rangle\langle h| \rho_s + \rho_s(|h\rangle\langle g|g\rangle\langle h|))\Big)$$
$$+ \sum_{\omega>0} \Gamma_h(-\omega)\Big(|h\rangle\langle g| \rho_s |g\rangle\langle h| - \frac{1}{2}(|g\rangle\langle h|h\rangle\langle g| \rho_s + \rho_s |g\rangle\langle h|h\rangle\langle g|)\Big). \tag{4.14}$$

Following the same procedure for the other dissipators, we obtain

$$\mathcal{D}_h(\rho_s) = \Gamma_h(\omega_h)\Big(\rho_s^{hh} |g\rangle\langle g| - \frac{1}{2}\big\{|h\rangle\langle h|, \rho_s\big\}\Big) + \Gamma_h(-\omega_h)\Big(\rho_s^{gg} |h\rangle\langle h| - \frac{1}{2}\big\{|g\rangle\langle g|, \rho_s\big\}\Big) \tag{4.15}$$

$$\mathcal{D}_c(\rho_s) = \gamma_c(\omega_c)\Big(\rho_s^{cc} |g\rangle\langle g| - \frac{1}{2}\big\{|c\rangle\langle c|, \rho_s\big\}\Big) + \Gamma_h(-\omega_c)\Big(\rho_s^{gg} |c\rangle\langle c| - \frac{1}{2}\big\{|g\rangle\langle g|, \rho_s\big\}\Big) \tag{4.16}$$

$$\mathcal{D}_w(\rho_s) = \Gamma_w(\Omega)\Big(\rho_s^{hh} |c\rangle\langle c| - \frac{1}{2}\big\{|h\rangle\langle h|, \rho_s\big\}\Big) + \gamma_w(-\Omega)\Big(\rho_s^{cc} |h\rangle\langle h| - \frac{1}{2}\big\{|c\rangle\langle c|, \rho_s\big\}\Big). \tag{4.17}$$

Now, we are going to study the diagonal terms of the evolution master equation. First, for all diagonal terms we have

$$\langle\epsilon| [H_s, \rho_s] |\epsilon\rangle = \langle\epsilon| H_s\rho_s |\epsilon\rangle - \langle\epsilon| \rho_s H_s |\epsilon\rangle = (\epsilon - \epsilon)\langle\epsilon| \rho_s |\epsilon\rangle = 0. \tag{4.18}$$

Using the notation $\rho_s^{ii} = \rho_s^i$ and equations 4.15, 4.16, 4.17 we will compute some relevant expectation values of the bath dissipators in the three levels energy eigenbasis. First, we obtain explicit $\dot{\rho}_s^g$ and then we apply the same procedure for the other terms.

- $\langle \mathbf{g} | \dot{\rho}_\mathbf{s} | \mathbf{g} \rangle$ term:

We have that

$$
\begin{aligned}
\langle g | \mathcal{D}_h(\rho_s) | g \rangle &= \Gamma_h(\omega_h)\left(\rho_s^h \langle g|g \rangle \langle g|g \rangle - \frac{1}{2}(\langle g|h \rangle \langle h| \rho_s |g \rangle + \langle g| \rho_s |h \rangle \langle h|g \rangle) \right) \\
&+ \Gamma_h(-\omega_h)\left(\rho_s^g \langle g|h \rangle \langle h|g \rangle - \frac{1}{2}(\langle g|g \rangle \langle g| \rho_s |g \rangle + \langle g| \rho_s |g \rangle \langle g|g \rangle) \right) \\
&= \Gamma_h(\omega_h)\rho_s^h - \Gamma_h(-\omega_h)\rho_s^g
\end{aligned}
\tag{4.19}
$$

$$
\begin{aligned}
\langle g | \mathcal{D}_c(\rho_s) | g \rangle &= \Gamma_c(\omega_c)\left(\rho_s^c \langle g|g \rangle \langle g|g \rangle - \frac{1}{2}(\langle g|c \rangle \langle c| \rho_s |g \rangle + \langle g| \rho_s |c \rangle \langle c|g \rangle) \right) \\
&+ \Gamma_c(-\omega_c)\left(\rho_s^g \langle g|c \rangle \langle c|g \rangle - \frac{1}{2}(\langle g|g \rangle \langle g| \rho_s |g \rangle + \langle g| \rho_s |g \rangle \langle g|g \rangle) \right) \\
&= \Gamma_c(\omega_c)\rho_s^c - \Gamma_c(-\omega_c)\rho_s^g
\end{aligned}
\tag{4.20}
$$

and

$$
\langle g | \mathcal{D}_w(\rho_s) | g \rangle = 0.
\tag{4.21}
$$

Hence, all the diagonal terms of the master equation are

$$
\begin{aligned}
\langle g | \dot{\rho}_s | g \rangle &= -\left(\Gamma_c(-\omega_c) + \Gamma_h(-\omega_h) \right)\rho_s^g + \Gamma_c(\omega_c)\rho_s^c + \Gamma_h(\omega_h)\rho_s^h \\
\langle c | \dot{\rho}_s | c \rangle &= (\Gamma_c(-\omega_c)\rho_s^g - \left(\Gamma_c(\omega_c) + \Gamma_w(-\omega_w) \right)\rho_s^c + \Gamma_w(\omega_w)\rho_s^h \\
\langle h | \dot{\rho}_s | h \rangle &= \Gamma_h(-\omega_h)\rho_s^g + \Gamma_w(\omega_w)\rho_s^c - \left(\Gamma_h(\omega_h) + \Gamma_w(\omega_w) \right)\rho_s^h.
\end{aligned}
\tag{4.22}
$$

It's important to note that in the previous equations the populations and coherences of the system evolve separately. If we write the dynamics of the populations in matrix form it follows that

$$
\begin{pmatrix} \dot{\rho}_s^g \\ \dot{\rho}_s^c \\ \dot{\rho}_s^h \end{pmatrix} = \begin{pmatrix} -\Gamma_c^- - \Gamma_h^- & \Gamma_c^+ & \Gamma_h^+ \\ \Gamma_c^- & -\Gamma_c^+ - \Gamma_w^- & \Gamma_w^+ \\ \Gamma_h^- & \Gamma_w^- & -\Gamma_h^+ - \Gamma_w^+ \end{pmatrix} \begin{pmatrix} \rho_s^g \\ \rho_s^c \\ \rho_s^h \end{pmatrix}.
\tag{4.23}
$$

Note that we are using the notation $\Gamma_\alpha(\pm\omega_\alpha) = \Gamma_\alpha^\pm$

4.3 The steady state

Now, we are going to study what happens when the system reaches a stationary state, *i.e.* when

$$\dot{\rho}_s = 0 \quad \text{with} \quad Tr\rho_s = 1. \tag{4.24}$$

Using the notation $\rho_s^i = \rho_{ss}^i$ for the steady state, the heat currents are given by

$$J_\alpha = Tr(H_S D_\alpha \rho_{ss}). \tag{4.25}$$

Another way to obtain this equations is study the quantum thermodynamic version of the I-law. In general, if the system is coupled to different baths, the evolution of any system operator can be written in terms of the GKSL Markovian generator, so

$$\frac{d}{dt}O_s = -i\Big[H_S, O_s\Big] + \sum_\alpha \mathcal{D}_\alpha(O_s) + \frac{\partial O_s}{\partial t}. \tag{4.26}$$

If we replace O_s by H_S and take average of the previous expression

$$\frac{d}{dt}\langle H_s\rangle = \sum_\alpha \langle \mathcal{D}_\alpha(H_s)\rangle + \langle\frac{\partial H_s}{\partial t}\rangle. \tag{4.27}$$

We know from statistical mechanics that $\langle H_S \rangle$ correspond to the energy E_S of the system so

$$\frac{dE_S}{dt} = \sum_\alpha \langle \mathcal{D}_\alpha(H_s)\rangle + \langle\frac{\partial H_s}{\partial t}\rangle. \tag{4.28}$$

Using the time derivative of the I-law of thermodynamics

$$\frac{dE_S}{dt} = \sum_\alpha J_\alpha + P \tag{4.29}$$

We can extrapolate equation 4.29 to 4.28 and we obtain

$$J_\alpha = \langle \mathcal{D}_\alpha(H_s)\rangle \quad \text{and} \quad P = \langle\frac{\partial H_s}{\partial t}\rangle. \tag{4.30}$$

In the tricycle, the Hamiltonian of the system H_S does not depend on time, so $P = 0$ and for the steady state the energy of the system is conserved, so there is no heat accumulated in it. That means,

$$\frac{dE_S}{dt} = 0 \implies \sum_\alpha J_\alpha = 0. \tag{4.31}$$

The next stage is obtain the stationary heat currents as functions of the system populations ρ^i_{ss} at the steady state. Using equation 4.25 and the equation for the diagonal terms (eq. 4.22) , the hot heat current is

$$
\begin{aligned}
J_h &= \langle g| H_S \mathcal{D}_h |g\rangle + \langle c| H_S \mathcal{D}_h |c\rangle + \langle h| H_S \mathcal{D}_h |h\rangle = \epsilon_g \langle g| \mathcal{D}_h |g\rangle + \epsilon_c \langle c| \mathcal{D}_h |c\rangle + \epsilon_h \langle h| \mathcal{D}_h |h\rangle \\
&= \epsilon_g (\Gamma_h^+ \rho^h_{ss} - \Gamma_h^- \rho^g_{ss}) + \epsilon_h (-\Gamma_h^+ \rho^h_{ss} + \Gamma_h^- \rho^g_{ss}) = \Gamma_h^- \rho^g_{ss}(\epsilon_h - \epsilon_g) - \Gamma_h^+ \rho^h_{ss}(\epsilon_h - \epsilon_g) \tag{4.32}
\end{aligned}
$$

Applying the same method, all the heat currents are given in terms of the stationary state populations as

$$
\begin{aligned}
J_h &= \hbar\omega_h(\Gamma_h^- \rho^g_{ss} - \Gamma_h^+ \rho^h_{ss}) \\
J_c &= \hbar\omega_c(\Gamma_c^- \rho^g_{ss} - \Gamma_c^+ \rho^c_{ss}) \\
J_h &= \hbar\omega_w(\Gamma_w^- \rho^c_{ss} - \Gamma_w^+ \rho^h_{ss}) \tag{4.33}
\end{aligned}
$$

Now we have to obtain the steady state populations in terms of the rates Γ_α. Using the condition 4.24 for the stationary state, equation 4.22 establish the following system

$$
\begin{aligned}
-\left(\Gamma_c^- + \Gamma_h^-\right)\rho^g_{ss} + \Gamma_c^+ \rho^c_{ss} + \Gamma_h^+ \rho^h_{ss} &= 0 \\
\Gamma_c^- \rho^g_{ss} - \left(\Gamma_c^+ + \Gamma_w^-\right)\rho^c_{ss} + \Gamma_w^+ \rho^h_{ss} &= 0 \\
\Gamma_h^- \rho^g_{ss} + \Gamma_w^+ \rho^c_{ss} - \left(\Gamma_h^- + \Gamma_w^+\right)\rho^h_{ss} &= 0 \tag{4.34}
\end{aligned}
$$

with the condition

$$\rho^g_{ss} + \rho^c_{ss} + \rho^h_{ss} = 1. \tag{4.35}$$

Solving this system leads to the next steady state populations

$$\rho_{ss}^g = \frac{\Gamma_h^+\Gamma_w^- + \Gamma_c^+(\Gamma_h^+ + \Gamma_w^+)}{(\Gamma_h^- + \Gamma_h^+)(\Gamma_c^+ + \Gamma_w^-) + (\Gamma_c^+ + \Gamma_h^-)\Gamma_w^+ + \Gamma_c^-(\Gamma_h^+ + \Gamma_w^- + \Gamma_w^+)}$$

$$\rho_{ss}^c = \frac{\Gamma_h^-\Gamma_w^+ + \Gamma_c^-(\Gamma_h^+ + \Gamma_w^+)}{(\Gamma_h^- + \Gamma_h^+)(\Gamma_c^+ + \Gamma_w^-) + (\Gamma_c^+ + \Gamma_h^-)\Gamma_w^+ + \Gamma_c^-(\Gamma_h^+ + \Gamma_w^- + \Gamma_w^+)}$$

$$\rho_{ss}^h = \frac{\Gamma_c^+\Gamma_h^- + (\Gamma_c^- + \Gamma_h^-)\Gamma_w^-}{(\Gamma_h^- + \Gamma_h^+)(\Gamma_c^+ + \Gamma_w^-) + (\Gamma_c^+ + \Gamma_h^-)\Gamma_w^+ + \Gamma_c^-(\Gamma_h^+ + \Gamma_w^- + \Gamma_w^+)}. \tag{4.36}$$

Using the Kubo-Martin-Schwinger(KMS) condition [11] for the transition rates $\Gamma_\alpha(\omega_\alpha) = e^{-\omega_\alpha/T_\alpha}\Gamma_\alpha(-\omega_\alpha)$ we can incorporate equations 4.36 in 4.33 and obtain that the steady heat currents in natural units ($\hbar = 1$) are given in terms of a flux I by

$$
\begin{aligned}
J_c &= \omega_c I \\
J_h &= -\omega_h I \\
J_w &= \omega_w I
\end{aligned}
\tag{4.37}
$$

where the flux I for a quantum tricycle is

$$I = \frac{\Gamma_c\Gamma_h\Gamma_w(e^{-\omega_w/T_w}e^{-\omega_c/T_c} - e^{-\omega_h/T_h})}{\Gamma_h\Gamma_c\left[e^{-\omega_c/T_c} + (1 + e^{-\omega_h/T_h})(1 + e^{-\omega_c/T_c})\right] + \Gamma_w(\Gamma_c + \Gamma_h e^{-\omega_h/T_h}) + \Gamma_c\Gamma_w e^{-\omega_c/T_c}(1 + e^{-\omega_w/T_w})}. \tag{4.38}$$

Using equations 4.37 and the constrain $\omega_w = \omega_h - \omega_c$ we can prove that the I-law is satisfied

$$J_c + J_h + J_w = (\omega_c - \omega_h + \omega_w)I = 0. \tag{4.39}$$

As we can realize, this flux is different from the quantum three level maser. This is because the maser is periodically driven by an external field and the work reservoir of our tricycle vanish. To obtain 2.18 we have to apply another Floquet theory which is reviewed according to our purposes in references[29, 30, 32, 36].

However, this chapter has been useful to apply the markovian master equation and obtain the heat currents in the steady state for a quantum tricycle. This exercise is useful to gain

understanding od the basic operation of thermal machines and the objects used to study them. A more detail analysis of this system, similar to the realized in Chapter 2, has been done in reference [19].

Chapter 5

Conclusions

The challenge of obtaining an thermal machine optimized in terms of its output power instead of its efficiency is one of our aims in this review. We have obtain the CA efficiency and introduce endoreversible machines by doing a similar derivation to the one followed in [25]. These result can be criticised [25] but, as discussed in reference [37], it is a good approximation for the efficiencies of different power plants. Then we have focused on the performance of one of the simplest model of quantum endoreversible thermal machine: the Three-Level Maser. We have defined two thermodynamics forces associated with each bath (hot and cold) and in contrast to other references as [26] , only one of them has been chosen as our control parameter. In particular, the optimization has been performed on the values of the cold thermodynamic force. Considering a generic model of endoreversible machine, we have shown that for the normalized efficiency η^E/η_C, in the case of linear flux, the value $1/2$ is reached, illustrating the universality of efficiency at maximum power for linear response [26]. By comparison, we have showed that normalized COP ϵ^R/ϵ_C, saturates to $1/2$ in the case of vanishing COP. For higher orders of the flux, we have prove that normalized efficiency η^E/η_C saturates to the fixed value $1/2$ always in the case of vanishing η_C but normalized COP saturates to different values. Nevertheless, additional assumptions about irreversibility should be considered to perform more practical machines. These assumptions and its effect has been studied in references [22, 37].

The theory of open quantum systems is fundamental and necessary to give an introduction about quantum thermodynamics. Hence, we have proceed with the derivation of the Markovian master equation in the weak coupling limit (WCL) following the seminal work on theory of open quantum system [11]. Doing some approximations, Born-Markov approximation and RWA, we have obtain the Markovian quantum master equation in the GKLS form. We have follow the WCL but in [11] other limits are considered.

To end our work, we have considered convenient to study the Markovian master equation for a specific system. There are several exactly solvable models [11, 38] but we have chosen the three level system as working example [29, 30, 32, 36]. We have analyzed the quantum tricycle with a three level system, also called quantum absorption refrigetator. In this case we have used this system to illustrate some common methods used in Quantum Thermodynamics, in particular, the used of Markovian master equations. In particular, under the Markovian assumption the GKLS equation is such that the populations and coherences evolves separately. To finish we have moved to the study of the steady state of the system and obtained the steady heat currents. In references [16, 19, 32] this and other models of quantum absorption refrigerators has been extensively studied.

Through this work, we have tried to bring the reader an academic introduction to the emerging field of Quantum Thermodynamics focusing on one of the subjects of interest, the operation of quantum thermal machines. To achieve our aim we have made a bibliographic review of different papers already mentioned. However, other works, see for instance [15], give a more complete view, including many issues treated in Quantum Thermodynamics and Quantum Information theory. We have not mentioned the Quantum Thermodynamics version of the III-law [10] and its implication and we also have not treated the important subject of the work fluctuation theorems [15].

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