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Ciclo de Otto não-adiabático para dois q-bits com interação isotrópica

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Dissertação de Mestrado apresentado ao Programa de Pós-Graduação em Física da Universidade Federal Fluminense como pré-requisito para obtenção do título de Mestre em Física.

ORIENTADOR: Prof. Dr.Antonio Zelaquett Khoury

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Dedicatória

Em memória de meu pai, Nelson Henrique de Moraes Duriez.

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Resumo

Nesta dissertação investigamos as propriedades termodinâmicas de um motor quântico formado por um par de q-bits interagentes, operado em um ciclo de Otto. A interação térmica ocorre com dois banhos a temperaturas distintas, enquanto o trabalho está relacionado a uma interação com um campo magnético com dependência temporal explícita e arbitrária. Para o acoplamento, consideramos o modelo de Heisenberg 1-d isotrópico, que nos permite descrever o sistema em termos da álgebra de Lie su(2). Apesar da dinâmica do motor só estar definida uma vez que o protocolo do campo magnético tenha sido estabelecido, nós mostramos que, ao fazer considerações sobre as temperaturas e frequências do ciclo, podemos concluir aspectos gerais à respeito das regiões de operações da máquina, especialmente como sobre como elas podem ser reduzidas ou até eliminadas para diferentes valores da constante de acoplamento. Por fim, nós investigamos numericamente como o trabalho extraído e a eficiência do motor podem mudar, ao considerarmos protocolo específico de transição da frequência de Rabi, para diferentes velocidades do protocolo, interpolando entre os limites adiabático e abrupto, para o quais recuperamos resultados originais.

Abstract

In this dissertation we investigate the thermodynamic properties of an engine formed by two coupled q-bits performing an Otto cycle. The thermal interaction occurs with two baths at different temperatures, while work is associated with the interaction with an arbitrary time-dependent magnetic field that varies in intensity and direction. For the coupling we consider the 1-d isotropic Heisenberg model, which allows us to describe the system by means of a su(2) Lie algebra. Although the time evolution of the engine is defined only once the protocol for the magnetic field has been established, we show that, by making some considerations about the temperatures and frequencies of the cycle, we can conclude general aspects about the operating regions of the engine, especially how they can be reduced or even eliminated for different values of the coupling parameter. Finally, we numerically investigate how the work output and the engine efficiency can change under a Rabi frequency transition for different transition rates interpolating the abrupt and adiabatic limits, from which we recover previous results.

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Introduction

The theory of classical thermodynamics is, without question, one of the most successful in all of physics. First formulated in the XVIII and XIX centuries by Carnot, Clausius, Maxwell, Boltzmann, Gibbs, and many others, it has served a great purpose in the industrial revolution by allowing us to describe and also construct more efficient thermal machines.

Despite its initial motivation, the scope of thermodynamics goes far beyond the study of machines. Indeed, one of the beauties of the subject is that it can describe an immense range of phenomena using only a reduced number of parameters, like the entropy, temperature and volume [2].

The success of the phenomenological descriptions provided by this formalism was so great that, in the present day, the laws of thermodynamics occupy a higher place in the hierarchy of physical theories, in a sense that all new theories must agree with the established principles of conservation of energy and entropy increase.

The field of quantum thermodynamics has emerged in the recent time, partially, as an attempt to recover, or reformulate, the laws of thermodynamics and some concepts like, heat, work and entropy by starting within a full quantum perspective. Not surprisingly, the analysis of driven quantum systems in contact with thermal environments has led to interesting results when made through a thermodynamic inspired framework. In 1959, Scovil and Schulz-Dubios described how a three level maser can be equivalent to a Carnot Engine, in a work that today is considered a seminal paper [3].

Motivated by this and other important results, the study of quantum thermal machines has flourished. Today there is a great variety of theoretical and experimental descriptions of these objects that seek to exploit the quantum nature of matter to

improve the performance of tasks in general. One of the reasons for the growing of the field is the direct connection to the development of more efficient quantum devices, which have received much attention in the last decade.

One possible scenario to idealize a quantum thermal machine is the one of spin systems controlled by external magnetic fields. Considering the spins as the working substance, protocols where the external magnetic field changes in time can be considered as work protocols in the quantum thermodynamics framework that will be described here. One of the first descriptions of a thermal machine composed of a single spin system was proposed in 1991 by Kosloff [4]. A few years later, the same author analyzed the case of interacting spins, where he explored the effects of *internal friction* associated with the interaction between the spins [5]. In 2011, Thomas and Johal described an Otto cycle of interacting spins following the 1-d isotropic Heisenberg Hamiltonian [6], but they considered a magnetic field varying only in intensity, with a fixed direction, which causes the Hamiltonian to commute at different times. In 2019, Campisi *et al.* considered a machine composed of a single spin but with a magnetic field varying in all three directions [1]. Other descriptions of thermal machines of spins systems can be found at [7],[8],[9],[10],[11],[12].

In this work we start in chapter 1 by presenting the quantum formalism to describe systems with time-dependent Hamiltonians, which are used as the working substance for quantum thermal machines. We show how some constraints on the commutation properties of the Hamitlonian can simplify or complicate the generated dynamics. We also describe under what circumstances the dynamics can be considered *adiabatic*, a regime that will be considered often throughout the description. To avoid confusion we differ quantum adiabatic processes, that occur without inducing transitions between the instantaneous eigenstates, from adiabatic processes in thermodynamics which occur in the absence of heat exchanges. We use q-adiabatic for quantum adiabatic processes and t-adiabatic for the case of thermodynamics. In chapter 1 we also present the algebraic method that is used in the numerical calculations of the time-evolution operator associated with these time-dependent systems, which was first presented in [13].

In chapter 2 we proceed by introducing the field of quantum thermodynamics and

showing how to define important quantities like work and heat within a quantum perspective, while reviewing some important results. To this day, a definition of quantum work and heat that is valid in all regimes has not been found, and therefore we present definitions that work only in some restrict cases, and we explore the realms of validity of the discussed definitions.

In chapter 3 we review in detail the description of a quantum thermal machine for a single spin (or q-bit) system. Following the steps presented in [1], we show how to compute the heat, the work and the efficiency of this machine by a simple derivation. One advantage of this description is that it enables us to investigate protocols that are performed outside the adiabatic limit. Many references on q-bit engines consider only the adiabatic case, that is much simpler, since during the adiabatic driving of an initially thermal state the system remains at an equilibrium state at all times.

In chapter 4 we present our original contributions. We expand the formalism from [1] to the case of two interacting spins, and we describe the interaction by the 1-d isotropic Heisenberg model. We also consider the action of an external magnetic field with variable amplitude and direction in time, therefore we describe a more general case than the one presented in [6], where the authors consider the same interaction model but with a field fixed in one direction. Thanks to the algebraic methods employed, we are able to describe this system for arbitrary protocols, and we also verify the results of the mentioned references as limiting cases.

In the last chapter we present the final considerations of the work, and specially, we focus on how the description can be further generalized, by considering other definitions of heat and work as well as more complicated models for the working substance.

Chapter 1

Time-dependent Hamiltonians

In this chapter we discuss the dynamics of quantum systems generated by Hamiltonians with explicit time-dependence. For such systems the general description can become quite intricate. It is convenient, therefore, to divide the analysis in some important limiting cases. For the sake of completeness, we first review the most general case, which is known as the formal solution. We then proceed to analyze the limiting cases that arise from the commutation properties of the time-dependent Hamiltonian. We also discuss the cases when the time variation of the Hamiltonian is too fast or slow compared to its characteristic time-scales, which are called the sudden and adiabatic limits, respectively. We conclude the chapter with a review of the algebraic method, presented in [13], to describe the dynamics of systems with Hamiltonians that are linear combinations of generators of the su(2), su(1,1) or so(2,1) Lie algebras. That method will be useful in our future analysis of quantum thermal machines in chapters 3 and 4.

1.1   Formal solution and limiting cases

To describe the motion of a system driven by a time-dependent Hamiltonian, we must solve the Schroedinger equation, as in any quantum dynamics problem. In its traditional form, it reads

$$H(t)\left|\Psi(t)\right\rangle = i\hbar\frac{d}{dt}\left|\Psi(t)\right\rangle. \tag{1.1}$$

It is convenient to write this equation in terms of the *time-evolution operator* (TEO) [14]. This operator associates the state at some initial arbitrary instant t_0 to the state

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at some later time t. We first consider the case of an initial pure state. The TEO, denoted by $U(t, t_0)$ is then given by

$$|\Psi(t)\rangle = U(t, t_0) |\Psi(t_0)\rangle. \tag{1.2}$$

The Schroedinger equation can be rewritten in terms of the the TEO [14], it is

$$i\hbar \frac{\partial}{\partial t} U(t, t_0) = H(t)U(t, t_0), \tag{1.3}$$

with the initial condition $U(t_0, t_0) = \mathbb{1}$. This is a differential equation for the operator $U(t, t_0)$, given some time-dependent Hamiltonian $H(t)$.

More generally, if our knowledge of the system is limited by classical statistical randomness, or if the system is part of a larger system that we cannot fully describe, it is necessary to represent the state as a more complex mathematical object, namely, the *density operator*, $\rho(t)$ [15]. For some given initial condition $\rho(t_0)$, the density operator at later times can be found by the following similarity transformation:

$$\rho(t) = U(t, t_0) \rho(t_0) U^\dagger(t, t_0). \tag{1.4}$$

1.1.1   The Dyson series

In the general case, for some arbitrary $H(t)$, the solution of equation (1.3) is given by [14]

$$
\begin{aligned}
U(t, t_0) &= \mathbb{1} + \sum_{n=1}^{\infty} (-\frac{i}{\hbar})^n \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 ... \int_{t_0}^{t_{n-1}} dt_n H(t_1)H(t_2)...H(t_n) \\
&= \mathcal{T} \left[\exp\left\{ -\frac{i}{\hbar} \int_{t_0}^{t} H(t')dt' \right\} \right],
\end{aligned} \tag{1.5}
$$

which is called the *Dyson series*, or the formal solution of the Schroedinger equation. The symbol $\mathcal{T}$ denotes the time ordering operator, which acts on products of operators at different times and returns the product in a form where the operators evaluated at more recent times always acts from the left. For example, consider some generic Hamiltonian evaluated at two different instants t_1 and t_2. The action of the time-ordering operator on this quantity is

$$
\mathcal{T}[H(t_1)H(t_2)] = \begin{cases} H(t_1)H(t_2) & \text{if } t_1 < t_2 \\ H(t_2)H(t_1) & \text{if } t_1 > t_2. \end{cases} \tag{1.6}
$$

At first sight the Dyson series seems to be the definitive way to solve the dynamics of a time-dependent quantum system because of its generality. However, in most of the applications the calculations involving the Dyson series become very complex, and for this reason other approaches and approximations are sought. In fact, there are common constraints on the properties of the Hamiltonian that greatly simplify the dynamics, and for these cases we can avoid the intricate calculations of the formal solution. We review some of these limiting cases in the rest of this chapter.

1.1.2 H(t) commutes at different times

Since the Hamiltonian is a Hermitian operator, it must have a complete set of orthonormal eigenstates and real eigenvalues at all times. We define this *instantaneous eigenstates* by the following eigenvalue equation

$$H(t)\left|\psi_n(t)\right\rangle = E_n(t)\left|\psi_n(t)\right\rangle.\tag{1.7}$$

Despite the resemblance with the time-independent Schroedinger equation, the states $\{\left|\psi_n(t)\right\rangle\}$ are not the solutions for the time-dependent case. However, we can obtain great insight if we analyze the dynamics in the basis spanned by the set $\{\left|\psi_n(t)\right\rangle\}$. An important case to consider is the one where the Hamiltonian commutes with itself at different times, or

$$[H(t), H(t')] = 0, \quad \forall(t, t').\tag{1.8}$$

If this is the case, then the action of the time ordering operator on a product such as the one on equation (1.6) will not change anything, since $H(t_1)H(t_2)$ and $H(t_2)H(t_1)$ will represent the same quantity. We can use this property to obtain the time evolution operator for this type of system. Since the time ordering operator acts as the identity we can simply remove it from expression (1.5) to get

$$U(t, t_0) = \exp\left\{-\frac{i}{\hbar}\int_{t_0}^{t} H(t')dt'\right\}.\tag{1.9}$$

One important feature of this kind of Hamiltonian is that the dynamics occurs without inducing transitions between the energy eigenstates. To see this, consider a system that obeys (1.8) with $H(t)$ having some set of eigenvectors obeying equation

(1.7). If the system starts the evolution in some arbitrary energy eigenstate $|\psi_n\rangle$, the state at later times can be found from equation (1.2) to be

$$|\Psi(t)\rangle = \exp\left\{ -\frac{i}{\hbar} \int_{t_0}^{t} H(t')dt' \right\} |\psi_n\rangle \tag{1.10}$$

$$= \exp\left\{ -\frac{i}{\hbar} \int_{t_0}^{t} E_n(t')dt' \right\} |\psi_n\rangle .$$

We can see that the energy eigenstates evolve only through a global phase factor that does not change the physical predictions of measurements done on the system. We can see that for this special type of Hamiltonian, if the system starts in an energy eigenstate, it will remain on this eigenstate throughout the whole evolution and there will be no transitions between energy eigenstates. From this brief discussion we can conclude that only Hamiltonians that do not commute at different times can induce transitions.

In the simplest and most known case of a time-independent Hamiltonian, we can factorize the Hamiltonian out of the integral in 1.9 to get

$$U_{const}(t, t_0) = \exp\left\{ -\frac{i}{\hbar} H \int_{t_0}^{t} dt' \right\} \tag{1.11}$$

$$= \exp\left\{ -\frac{i}{\hbar} H(t - t_0) \right\},$$

and the phase added to the energy eigenstates is $e^{-iE_n(t-t_0)}$. This solution is the usual one dealt with in graduate quantum mechanics textbooks.

1.1.3 The sudden and adiabatic limits

We have seen a constraint on the commutation properties of the time-dependent Hamiltonian that greatly simplifies the dynamics. We can have two other simple limiting cases if we analyze the speed in which the time-variation of the Hamiltonian takes place. For infinitely slow, or quasi-static protocols, we have the *adiabatic regime*, which is characterized by a transitionless dynamics. On the other hand, the time-variation of the Hamiltonian can be infinitely fast, or abrupt. We name this the *sudden regime*. This type of dynamics is usually reffered in the literature [16] as a "sudden quench" in the Hamiltonian.

In order to speak of these two regimes we must first define quantitatively what do we mean by "fast" or "slow" processes. For the sake of simplicity, we proceed the analysis for the case of a system with discrete energy levels, finite dimension and a set of instantaneous energy eigenstates as in equation (1.7). The typical time-scale for the dynamics of expectation values of observables, and therefore for the system as a whole, is given by the *Böhr frequencies* [15], which depend on the spacing between the energy levels at a fixed time. For two time-dependent energy levels $,E_n(t)$ and $E_m(t)$, the instantaneous Bohr frequencies are given by

$$f_{mn}(t) = \frac{|E_n(t) - E_m(t)|}{h}, \tag{1.12}$$

where h is Planck's constant. In the literature [15], the Bohr frequencies are defined for time-independent systems, and we have defined this instantaneous version for the sake of the argument regarding the sudden and adiabatic limits. The characteristic time associated with this pair of energy levels, or this particular *transition* between energy eigenstates, is

$$\tau_{mn}(t) = \frac{1}{f(t)} = \frac{h}{|E_n(t) - E_m(t)|}. \tag{1.13}$$

The shortest natural time-scale of the system will be associated with the largest Bohr frequency, if we maximize it over all pairs of energy levels along the dynamics. This time interval, which we call τ_s, is then given by

$$\tau_{\mathrm{s}} = \min_{t,m,n} \tau_{mn}(t). \tag{1.14}$$

By the same reasoning, the largest time-scale will be associated with the smallest Böhr frequency, but now we must maximize the characteristic time over all pairs of energy levels during the dynamics. It is

$$\tau_{\mathrm{ad}} = \max_{t,m,n} \tau_{mn}(t). \tag{1.15}$$

Now that we defined the typical time-scales we can speak properly of "fast" or "slow" processes. Consider a Hamiltonian that changes from a constant one H_0 to another constant H_1 after some process that takes a time interval τ. For convenience, we refer to this time-interval as the *"sweep time"*. The dynamics will be in the

"sudden limit" if the sweep time is much shorter than the smallest characteristic time of the system, or $\tau \ll \tau_s$. Because the sweep time is negligible in this limit, we can consider that the Hamiltonian changes instantaneously from H_0 to H_1, and therefore the dynamics can be solved by composing the time-evolution operators associated with the part of the evolution governed by H_0 and H_1, respectively. As it is carefully explained in [17], "The final state of the system for the old Hamiltonian H_0 will be the initial state for the new Hamiltonian H_1". Since H_0 and H_1 are time-independent, the time-evolution operator for both parts can be straightforwardly found by using (1.11), and the complete TEO is the composition of these two contributions.

Imagine the situation where the system is in an eigenstate of H_0, with energy E_0, right before the sudden sweep. If $[H_0, H_1] \neq 0$, which is often the case, then the current eigenstate of H_0 will be a nontrivial superposition of eigenstates of H_1, with some set of nonzero amplitudes. After we apply the TEO associated with H_1, each of this amplitudes will evolve by a different relative phase, as it is described in equation (1.11). The resulting state after this evolution will not be, in general, an eigenstate of either H_0 or H_1. In this situation, if we measure the energy in the basis of H_0 at some later time after the sweep we will find a different result than E_0 with nonzero probability. Since we initially prepared the system with energy E_0, we can interpret this phenomenon as a *transition* between the energy levels caused by the abrupt change in the Hamiltonian.

These transitions induced by fast changes in the Hamiltonian appear in a wide range of physical systems. One interesting example is the quantum harmonic oscillator with a time-dependent frequency. If we take some harmonic oscillator prepared in its fundamental state and abruptly change its frequency, the resulting state after this protocol will inevitably be in a *vaccum squeezed state*, which is a superposition of all even energy eigenstates of the initial Hamiltonian. For a detailed discussion on this problem see [18].

Another limiting case, the *"adiabatic limit"*, occurs when the Hamiltonian changes very slowly compared to the system's characteristic timescales. In the aforementioned scenario, where the system's Hamiltonian changes from H_0 to H_1 in a sweep of time τ, the process will be adiabatic when the sweep time is much greater than the largest

characteristic time of the system, or $\tau \gg \tau_{ad}$. To understand what happens in this particular dynamics we can invoke the adiabatic theorem of quantum mechanics, a powerful and important result. It is possible to formulate this theorem in a variety of ways, and we choose a rather systematic and informal approach following the lecture notes in [19]. A detailed discussion can be found in [14]. The theorem can be stated using the notation given in equations (1.2) and (1.7).

Theorem: For a time-dependent Hamiltonian that is slowly varying between t_0 and t the transition probabilities between the instantaneous eigenstates of the Hamiltonian are highly supressed, and go to zero for infinitely slow protocols.

Mathematically, we have, for an infinitely slow process [19],

$$
U_{ad}(t, t_0) \left| \psi_n(t_0) \right\rangle = \exp\left\{ -\frac{i}{\hbar} \int_{t_0}^{t} E_n(t') dt' \right\} \exp\left\{ -\int_{t_0}^{t} \left\langle \psi_n(t') \middle| \dot{\psi}_n(t') \right\rangle dt' \right\} \left| \psi_n(t) \right\rangle .
$$
(1.16)

We can see that that the evolved eigenstate $\left| \psi_n(t_0) \right\rangle$ is proportional to the instantaneous eigenstate at time t, with two phase factors. The first phase is similar to the one obtained for a Hamiltonian that commutes with itself at different times, as in 1.10, and it is typical for any transitionless dynamics. The term $\left\langle \psi_n(t') \middle| \dot{\psi}_n(t') \right\rangle$ can be proven to be purely imaginary, and thus the second term is only a phase factor. This second phase is called the geometrical phase, and it has many interesting properties. One of the most important is that, for a cyclic evolution (one that begins and ends at the same state), this phase depends only on the geometric properties of the dynamics in the parameter space of the Hamiltonian. For more information on geometric phases see [14].

Just like in the case of a Hamiltonian that commutes at different times, the dynamics in the adiabatic approximation takes place without inducing transitions between the instantaneous eigenstates, even when the Hamiltonian does not commute at different times.

There is another case that will be crucial on our future analysis of the quantum thermal machine, and that is the case when the Hamiltonian is a linear combination of the generators of the su(2), su(1,1) and so(2,1) Lie Algebras. Since this topic is not present in standart textbooks, we chose to describe the mathematics involved in this situation in detail. That is the concern of the next two sections.

1.2 The BCH-like relations

In quantum mechanics we often deal with exponentials of operators, (*e.g.* in eq. (1.11)). In these objects, when the exponent is a sum of operators that do not commute, the factorization is quite non trivial, as stated in [20]. However, when the operators in the exponent are generators of some particular Lie Algebra, there is an elegant way to proceed. Consider the operators satisfying

$$[T_-, T_+] = 2\epsilon T_c, \quad [T_c, T_\pm] = \pm\delta T_\pm. \tag{1.17}$$

These are the commutation relations for the $su(2,1)$, $su(2)$ and $so(2,1)$ Lie algebras. Parameters ϵ and δ are introduced in order to treat the three algebras in the same framework, and their values for the given algebras are indicated below.

Lie Algebra	ϵ	δ
$su(1,1)$	1	1
$su(2)$	-1	1
$so(2,1)$	$i/2$	i

Now consider the operator

$$G = f(\boldsymbol{\lambda}) = e^{\lambda_+ T_+ + \lambda_c T_c + \lambda_- T_-}, \tag{1.18}$$

where $\boldsymbol{\lambda} = (\lambda_+, \lambda_c, \lambda_-)$ is a set of complex parameters. Since the T operators are generators of the given algebras, the G operators are elements of the group associated with those algebras by the definition of the group structure [21]. For the algebras presented here, it can be shown that any group element as in equation (1.18) can also be written in a factorized form, as presented in [13].

$$G = h(\boldsymbol{\Lambda}) = e^{\Lambda_+ T_+} e^{\ln \Lambda_c T_c} e^{\Lambda_- T_-}. \tag{1.19}$$

The new set of parameters $\boldsymbol{\Lambda}$ is related to the old one by

$$\Lambda_c = \left(\cosh(\nu) - \frac{\delta\lambda_c}{2\nu}\sinh(\nu)\right)^{-\frac{2}{\delta}} \quad \text{and} \quad \Lambda_\pm = \frac{2\lambda_\pm \sinh(\nu)}{2\nu\cosh(\nu) - \delta\lambda_c\sinh(\nu)}, \tag{1.20}$$

with ν given by

$$\nu^2 = \frac{(\delta\lambda_c)^2}{2} - \delta\epsilon\lambda_+\lambda_-. \tag{1.21}$$

A proof of this result for the cases of the $su(1,1)$ algebra ($\delta = \epsilon = 1$) is given in [20], and the generalization for the other cases is presented in [13]. The relations between these sets of parameters are known in the literature as the "BCH-like relations", in reference to the Baker-Campbell-Hausdorff relation, that is used in the derivation of these results.

1.3 The New BCH-like relations

This section based on the work in [13]. Another result that is necessary to our future analysis is the composition of N group elements of the given algebras. Since these operators are elements of a group, their composition (or product, in this case) always yields another element of the group. Using the factorized representation of the G operators in eq. (1.19), we can write

$$
\begin{aligned}
G(\mathbf{\Lambda}_N)G(\mathbf{\Lambda}_{N-1})\cdots G(\mathbf{\Lambda}_2)G(\mathbf{\Lambda}_1) = \qquad\qquad\qquad\qquad\qquad (1.22)\\
= e^{\Lambda_{N+}T_+}e^{\ln(\Lambda_{Nc})T_c}e^{\Lambda_{N-}T_-}e^{\Lambda_{(N-1)+}T_+}e^{\ln\left(\Lambda_{(N-1)c}\right)T_c}e^{\Lambda_{(N-1)-}T_-}\cdots\\
\cdots\; e^{\Lambda_{2+}T_+}e^{\ln(\Lambda_{2c})T_c}e^{\Lambda_{2-}T_-}e^{\Lambda_{1+}T_+}e^{\ln(\Lambda_{1c})T_c}e^{\Lambda_{1-}T_-}\\
= e^{\alpha_N T_+}e^{\ln(\beta_N)T_c}e^{\gamma_N T_-}\;.\qquad\qquad\qquad\qquad\qquad
\end{aligned}
$$

We wish to know the parameters $(\alpha_N, \beta_N, \gamma_N)$ of the resulting element as a function of $\mathbf{\Lambda}_i = (\Lambda_{i+}, \Lambda_{ic}, \Lambda_{i-})$, with $(i = 1, 2, ..., N-1, N)$. Using mathematical induction, we first find the relations for the composition of two elements and then generalize to N elements. The composition of two elements, already in the factorized form, reads

$$
G(\mathbf{\Lambda}_2)G(\mathbf{\Lambda}_1) = e^{\Lambda_{2+}T_+}e^{\ln(\Lambda_{2c})T_c}e^{\Lambda_{2-}T_-}e^{\Lambda_{1+}T_+}e^{\ln(\Lambda_{1c})T_c}e^{\Lambda_{1-}T_-}\;. \qquad (1.23)
$$

To rewrite this expression as a single G operator we need to group together operators with the same generator in the exponent, for in this case we can add the exponents. We leave a detailed derivation of this composition in the Appendix. There, we find

$$
G(\mathbf{\Lambda}_2)G(\mathbf{\Lambda}_1) = e^{\alpha_2 T_+}e^{\ln(\beta_2)T_c}e^{\gamma_2 T_-}, \qquad (1.24)
$$

with

$$\alpha_2 = \Lambda_{2+} + \frac{\Lambda_{1+}(\Lambda_{2c})^\delta}{1 - \epsilon\delta\Lambda_{1+}\Lambda_{2-}},$$

$$\beta_2 = \frac{\Lambda_{1c}\Lambda_{2c}}{(1 - \epsilon\delta\Lambda_{1+}\Lambda_{2-})^{\frac{2}{\delta}}}, \qquad (1.25)$$

$$\gamma_2 = \Lambda_{1-} + \frac{\Lambda_{2-}(\Lambda_{1c})^\delta}{1 - \epsilon\delta\Lambda_{1+}\Lambda_{2-}}.$$

To proceed with the induction we compose a third element of the group, which means to operate another $G(\boldsymbol{\Lambda})$ operator from the left of equation (1.24). We get

$$G(\boldsymbol{\Lambda}_3)G(\boldsymbol{\Lambda}_2)G(\boldsymbol{\Lambda}_1) = G(\Lambda_{3+}, \Lambda_{3c}, \Lambda_{3-})G(\alpha_2, \beta_2, \gamma_2). \qquad (1.26)$$

As we can see, the right-hand side of the equation above is just another composition of two G operators. We can therefore use equations (1.24) and (1.25) to write

$$G(\boldsymbol{\Lambda}_3)G(\boldsymbol{\Lambda}_2)G(\boldsymbol{\Lambda}_1) = e^{\alpha_3 T_+}e^{\ln(\beta_3)T_c}e^{\gamma_3 T_-}, \qquad (1.27)$$

with

$$\alpha_3 = \Lambda_{3+} + \frac{\alpha_2(\Lambda_{3c})^\delta}{1 - \epsilon\delta\alpha_2\Lambda_{3-}},$$

$$\beta_3 = \frac{\beta_2\Lambda_{3c}}{(1 - \epsilon\delta\alpha_2\Lambda_{3-})^{\frac{2}{\delta}}}, \qquad (1.28)$$

$$\gamma_3 = \gamma_2 + \frac{\Lambda_{3-}(\beta_2)^\delta}{1 - \epsilon\delta\alpha_2\Lambda_{3-}}.$$

By inspection of the equation above and the equations in (1.25), we can see that the coefficients $(\alpha_3, \beta_3, \gamma_3)$ depend on $(\alpha_2, \beta_2, \gamma_2)$ in the exact same way as the latter depends on $(\Lambda_{1+}, \Lambda_{1c}, \Lambda_{1-})$. If we were to compose a fourth operator, the new coefficients would still be the same functions of the previous ones by the same reasoning presented in equations (1.26) and (1.27). The same would be true for a fifth operator, and so on. This pattern allows us to build recurrence relations for the coefficients of the G operator resulting from the composition of N group elements. We have

$$G(\boldsymbol{\Lambda}_N)G(\boldsymbol{\Lambda}_{N-1})\cdots G(\boldsymbol{\Lambda}_2)G(\boldsymbol{\Lambda}_1) = e^{\alpha_N T_+}e^{\ln(\beta_N)T_c}e^{\gamma_N T_-} \qquad (1.29)$$

$$\alpha_N = \Lambda_{N+} + \frac{\alpha_{(N-1)}(\Lambda_{Nc})^\delta}{1 - \epsilon\delta\alpha_{(N-1)}\Lambda_{N-}},$$

$$\beta_N = \frac{\beta_{(N-1)}\Lambda_{Nc}}{(1 - \epsilon\delta\alpha_{(N-1)}\Lambda_{N-})^{\frac{2}{\delta}}}, \qquad (1.30)$$

$$\gamma_N = \gamma_{(N-1)} + \frac{\Lambda_{N-}(\beta_{(N-1)})^\delta}{1 - \epsilon\delta\alpha_{(N-1)}\Lambda_{N-}}.$$

with $\alpha_1 = \Lambda_{1+}$, $\beta_1 = \Lambda_{1c}$ and $\gamma_1 = \Lambda_{1-}$. These results are the new BCH-like relations. An interesting fact is that the α_N coefficients, which are independent of γ_N and β_N, can be written in the elegant form

$$\alpha_j = \Lambda_{j+} - \cfrac{(\Lambda_{jc})^\delta}{\epsilon\delta\Lambda_{j-} - \cfrac{1}{\Lambda_{(j-1)+} - \cfrac{(\Lambda_{(j-1)c})^\delta}{\epsilon\delta\Lambda_{(j-1)-} - \cfrac{1}{\ddots \Lambda_{2+} - \cfrac{(\Lambda_{2c})^\delta}{\epsilon\delta\Lambda_2 - -\frac{1}{\Lambda_{1+}}}}}}}. \qquad (1.31)$$

This expression is a generalized continued fraction (GCF). Objects like these appear in several different areas of mathematics, such as complex analysis and number theory. For more information on GCF's we suggest [22]. Because of the recursive nature of the calculation method presented, the numerical implementation is very straightforward.

1.4 Time evolution of time-dependent quantum systems

In this section we shall use the algebraic methods developed in the last section to present an alternative way to solve the equations of motion of quantum systems with time-dependent Hamiltonians in the special case when the Hamiltonian is a linear combination of the generators of the Lie algebras presented in table 1.2. Consider the time-dependent Hamiltonian given by

$$H(t) = \eta_+(t)T_+ + \eta_c(t)T_c + \eta_-(t)T_-. \qquad (1.32)$$

The coefficients $\boldsymbol{\eta}(t) = (\eta_+, \eta_c, \eta_-)$ are arbitrary complex functions of time and they carry all the time dependence of the Hamiltonian, since the generators of the Lie algebras (T operators) are assumed to be time-independent. For $H(t)$ to be Hermitian we must have η_c real and T_c Hermitian, as well as $T_+^\dagger = T_-$ and $\eta_+^* = \eta_-$. As for

any closed quantum system, the time evolution of the density operator between two instants t_0 and t is dictated by the Schroedinger equation, which can be cast in the form

$$\rho(t) = U(t, t_0)\, \rho(t)\, U^\dagger(t, t_0), \tag{1.33}$$

where U is the time evolution operator (TEO) defined in (1.3). We can see that the state of the system at any instant of time is completely determined once we have the TEO and the initial state. In the general case, however, the solution of the equation above is given by the Dyson series, which can be very difficult to treat mathematically.

Instead of the Dyson series, the authors in [13] have implemented a *time-splitting* approach, which consists in dividing the time-evolution in discrete steps of size τ. From the composition property of the time evolution operator, which comes from its definition [14], we can write

$$U(t, t_0) = U(t, t_{N-1})U(t_{N-1}, t_{N-2})\cdots U(t_1, t_0)\,, \tag{1.34}$$

where $t_j - t_{j-1} = \tau$, with $j = 1, ..., N - 1$. For arbitrary τ we do not gain any advantages since each operator on the right-hand side of (1.34) will be given by the solution of equation (1.3), and therefore by a Dyson series. However, if we make $\tau \to 0$, $N \to \infty$ and $t = N\tau$, we can treat the Hamiltonian as constant in each infinitesimal time interval. For constant Hamiltonians the TEO is easily computed (eq. (1.11) and we can write

$$U(t, t_0) = \lim_{\substack{N \to \infty \\ N\tau = t}} e^{-\frac{i}{\hbar}H(N\tau)\tau}e^{-\frac{i}{\hbar}H((N-1)\tau)\tau}\cdots\, e^{-\frac{i}{\hbar}H(\tau)\tau}\,. \tag{1.35}$$

For numerical implementations of this method we cannot make the time step τ infinitely small. It is sufficient, nonetheless, to choose the step to be much smaller then the typical time scale of the $\boldsymbol{\eta}(t)$ parameters of Hamiltonian. In this case, we can safely assume these parameters to be constant by parts in each one of the time steps.

Since all the relevant functions of time are treated as constant by parts, it is convenient to associate a discrete index to the time evolution. By doing so, the

parameters of the Hamiltonian become

$$\boldsymbol{\eta}(t) = \begin{cases} \boldsymbol{\eta}_0 & \text{for} & t \leq t_0 \\ \boldsymbol{\eta}_1 & \text{for} & 0 < t \leq \tau \\ \vdots & & \vdots \\ \boldsymbol{\eta}_j & \text{for} & (j-1)\tau < t \leq j\tau \\ \vdots & & \vdots \\ \boldsymbol{\eta}_N & \text{for} & (N-1)\tau < t \leq N\tau \end{cases}, \tag{1.36}$$

with $\boldsymbol{\eta}_j = (\eta_{j+}, \eta_{jc}, \eta_{j-})$. Without loss of generality, we can fix the values of the discrete version to coincide with the continuous one at the extreme values, $i.e.$, $\boldsymbol{\eta}_j := \boldsymbol{\eta}(j\tau)$. The same can be done to the Hamiltonian. We define

$$H_j = \eta_{j+} \, T_+ + \eta_{jc} \, T_c + \eta_{j-} \, T_- \, .$$

Since each H_j is constant in the limit of infinitesimal steps, the TEO for each step is given by

$$U_j := U(t_j, t_{j-1}) = e^{-\frac{i}{\hbar} H_j \tau} = e^{\lambda_{j+} T_+ + \lambda_{jc} T_c + \lambda_{j-} T_-}, \tag{1.37}$$

where $\boldsymbol{\lambda}_j = -\frac{i}{\hbar} \tau \boldsymbol{\eta}_j$.

Observe that U_j has the exact same form as the G operators presented in 1.18. We can, therefore, apply the aforementioned factorization procedure to get

$$U_j = e^{\Lambda_{j+} T_+} e^{\ln \Lambda_{jc} T_c} e^{\Lambda_{j-} T_-}, \tag{1.38}$$

where the relations between $\boldsymbol{\Lambda}$ and $\boldsymbol{\lambda}$ were given in equations (1.20) and (1.21).

Now we insert the factorized form of the TEO, for each time step in equation (1.35) to get

$$\begin{aligned} U(t, t_0) &= U_N \, U_{(N-1)} ... U_2 \, U_1 \tag{1.39} \\ &= \left\{ e^{\Lambda_{N+} T_+} e^{\ln(\Lambda_{Nc}) T_c} e^{\Lambda_{N-} T_-} \right\} \cdot \left\{ e^{\Lambda_{(N-1)+} T_+} e^{\ln(\Lambda_{(N-1)c}) T_c} e^{\Lambda_{(N-1)-} T_-} \right\} \cdots \\ &\cdots \left\{ e^{\Lambda_{2+} T_+} e^{\ln(\Lambda_{2c}) T_c} e^{\Lambda_{2-} T_-} \right\} \left\{ e^{\Lambda_{1+} T_+} e^{\ln(\Lambda_{1c}) T_c} e^{\Lambda_{1-} T_-} \right\}. \end{aligned}$$

We have shown that the TEO of the system of interest can be written as a sequence of products of G operators in the factorized form, one for each infinitesimal time step. This is exactly the same situation we encountered in section 1.2, when we discussed

the composition rule for elements of the given Lie groups. We can, therefore, use equation (1.22) to rewrite the TEO in the final form, namely

$$U(t, t_0) = e^{\alpha_N T_+} e^{\ln(\beta_N) T_c} e^{\gamma_N T_-}, \tag{1.40}$$

where the coefficients $(\alpha_N, \beta_N, \gamma_N)$ are given in equation (1.30). This result tells us that the TEO of a system with a time dependent Hamiltonian that is a combination of generators of the given Lie algebras can always be written as a product of exponentials of a single generator. The recursive relations for the coefficients mentioned above are very well suited for numerical implementations, and they have been used in [23] to successfully describe the dynamics of harmonic a oscillator with a time-dependent frequency.

We have presented the methods to describe systems with time-dependent Hamiltonians, and now we show how this type of system can describe the working substance for thermodynamic processes.

Chapter 2

Quantum Thermodynamics and Quantum Work

In this chapter we introduce the topic of quantum thermodynamics, as well as definitions of work and heat in a quantum context.

In classical physics, the concept of work is one of the most fundamental and well stablished concepts. Its formal definition comes from classical mechanics, and is given by the expression

$$W = \int_C \vec{F} \cdot d\vec{r}, \tag{2.1}$$

where $\vec{F}$ is the resultant force and $d\vec{r}$ is the infinitesimal displacement along the trajectory C. This simple definition can be translated to describe other forms of work appearing in all other areas of classical physics, such as thermodynamics, electromagnetism and statistical mechanics. Because this concept has been extensively used for more than a century, it is possible to not notice the beauty of the following fact: There is one, completely general definition of work that serves all purposes in classical physics.

By looking closely at expression (2.1), it becomes clear why it is difficult, at first sight, to define work in quantum mechanics, since objects such as forces and trajectories are not clearly defined in the theory. Differently from classical mechanics, there is not a general definition of quantum work known to this day.

There are, nevertheless, some definitions that are valid on specific regimes, and we review one of them, that emerges from the two-point measurement protocol, and obeys well verified fluctuation relations. We also discuss under what conditions this

definition is valid.

2.1   Work in thermodynamics

The concept of work appears in classical thermodynamics as a process of energy exchange that is done in a controlled and agent-based fashion. Formally, it is an energy flow that is associated with the variation of the extensive parameters of the system [2], such as the volume of a piston, if we are dealing with a gas, or the external magnetic field, for spin systems. In the context of thermal machines, specifically heat engines, work is usually thought as the energy that can be extracted from the temperature gradient between two heat reservoirs, with the goal of performing some task, such as expanding a piston. If we speak of a refrigerator, work can then be understood as the amount of energy that needs to be invested in the system in order to make the heat flow from a cold reservoir to a hot one.

In general, not all work applied to a system can be fully converted into useful energy to perform the given task. Some part of it will inevitably dissipate to microscopic (not extensive) degrees of freedom, which makes the process irreversible. Usually, this dissipation is on the form of heat. This is a manifestation of the second law of thermodynamics, that can be formulated in terms of the work applied and the Helmholtz free energy difference. This convenient form of this law reads

$$W \geq \Delta F, \tag{2.2}$$

with the equality being valid only for reversible processes. The free energy difference is the part of the work that can be stored in an accessible degree of freedom of some system, and can be later used to perform the given task. For example, the free energy difference can be used to lift some mass from the ground, therefore storing the energy as gravitational potential energy. We can see that the equation above tells us that the more irreversible the process, the more work is needed to obtain the same amount of accessible energy. All the laws of classical equilibrium thermodynamics, such as the one presented above, are known to be valid only in the thermodynamic limit, when the number of particles and excitations becomes very large, as much as Avogadro's number, 6.0221409×10^{23}.

It is possible to formulate the same laws in the viewpoint of statistical mechanics. In this theory, all quantities are described, not by deterministic values, but as stochastic variables that fluctuate around a mean value according to some probability distribution that depends on the type of ensemble analyzed. One of the greatest theoretical advances given by this theory is that it recovers all the results of standart thermodynamics for the mean values of the macroscopic quantities. These averages correspond precisely to the observed, deterministic, thermodynamic variables because the fluctuations around the mean values become negligible in comparison with their respective average values in the thermodynamic limit.

2.2   Classical Jarzynski's equality

We can also reformulate concepts of thermodynamics, such as heat and work, in the context of systems with a small number of constituents. These systems are described in the field of *stochastic thermodynamics*. In this scenario the thermodynamic limit is no longer valid and it is necessary to take into account fluctuations in the thermodynamic variables. This is when the fluctuation relations come into play.

To introduce this topic consider the following procedure: We initially prepare some general system in equilibrium with a thermal reservoir (or *bath*) at inverse temperature $\beta = \frac{1}{k_b T}$. Notice that this system does not need to be in the thermodynamic limit, meaning that it can have a small number of degrees of freedom. One possible example would be a system consisting of a single spin in contact with a thermal bath.

We then apply some force protocol by changing some extensive parameter, or set of parameters, of the system. As an important aspect, if the work protocol is not reversible the state resulting from it will be, in general, a non-equilibrium one.

Now suppose we make a measurement of the work done in this protocol. In the classical case, there are no issues in defining and measuring this work, and the measurement will not change the characteristics of the system in any way, in principle. If we perform this procedure many times, the measured work will fluctuate considerably, due to the absence of the thermodynamic limit, in which fluctuations on quantities like internal energy, heat and work become too small compared to their respective average values. It is necessary, therefore, to speak of a *work probability distribution,*

$P(W)$. The average work can be calculated from this distribution by the usual law,

$$\langle W \rangle = \int W P(W) dW. \tag{2.3}$$

In the thermodynamic limit, the values of the work measurements in each trial should approach the average value. It is important to note that the average symbols in the expression above indicate ensemble avareges over many trials of the protocol, and these trials can be made for protocols arbitrarily far from equilibrium.

After the measurement, the system is left to thermalize with the bath, arriving at another equilibrium state at the same temperature as before, but now the state is different because the extensive parameters have changed. It is possible to compute the free energy difference between the initial and final equilibrium states since the free energy is a state function. For macroscopic systems equation (2.1) says that the work done will be different from the free energy difference if the process is not reversible, and this is all the information this law gives us since classical thermodynamics does not provide equalities for non-equilibrium processes. The celebrated result by Jarzynski [24] relates the work done in the force protocol with the free energy difference for microscopic systems by the following equality:

$$\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}. \tag{2.4}$$

The average sign in the left hand side indicates ensemble averages over many trials of the experiment, in the same way as in equation (2.3).

Here we have considered that after the work protocol the system thermalizes with a bath with the same temperature as the one of the initial thermal state. Another case that will be interesting for our analysis of thermal machines is the one where the two baths considered have different temperatures. This temperature gradient between the two reservoirs is necessary to extract work from this system, in the same way as in the classical case [2].

There are many important aspects of Jarzynski's equality, and we briefly review some of them. First, in the right hand side, we have the free energy difference, which contains information about the initial and final equilibrium states. This means that this part of the equality is completely independent of the process that connects these states. In the left hand side, we have an average of an exponential function of the

work, a quantity that depends on the process, taken over trials that can be done far from equilibrium. This property allows us to obtain equilibrium information by performing work measurements of processes that involve non-equilibrium states, and it has been used to verify Jarzynski's equality experimentally for a RNA molecule that was repeatedly stretched and compressed [25]. The authors compared the average taken over irreversible processes with the already known free energy difference and have obtained a considerable agreement, therefore showing the validity of the theory described above.

We can use Jensen's inequality for convex functions, $\langle f(x) \rangle \geq f(\langle x \rangle)$, to directly recover the second law for the average work. Explicitly, we have

$$\langle W \rangle \geq \Delta F. \tag{2.5}$$

This means that the second law can be broken for individual trials of the experiment, but it must be valid for the average value of the work. We can see that this fluctuation theorem introduces the statistical nature of thermodynamic systems in a very natural and elegant way.

To end our discussion on the classical Jarzynski equality, we mention the only two assumptions that are made on its derivation, discussed in detail in [24]. The first one is that the system must be initially in a thermal state, or equivalently, to be described by a Gibbs ensemble. The second is that the system must obey the principle of microrreversibility, which means that the microscopic dynamics of the constituents of the system must satisfy the time-reversal symmetry, which is automatically true for conservative systems. Because of the few and very comprehensive assumptions, Jarzynski's equality is a very celebrated result in the field of non-equilibrium statistical mechanics and stochastic thermodynamics. Interestingly, these assumptions are also required to derive this result for quantum systems, but additional constraints are necessary. That is the topic of the next section.

2.3   The two-point measurement for work

The results discussed in the previous section have been derived for the quantum regime in [26] for the cases of an isolated system and a system in contact with a bath with

a specific master equation. We introduce a definition of work consistent with the quantum version of Jarzynski's equality in a more operational approach, inspired by [16]. We have chosen to illustrate this concept by a series of protocols done on a system, consisting on the following 4 steps.

Step 1: Given a quantum system described by a density operator $\rho(t)$ at the instant $t = t_0$, prepare it in a thermal state at inverse temperature β and with an initial Hamiltonian H_0. The density operator will then be given by the usual Gibbs state

$$\rho(t_0) \equiv \rho_0^{th} = \frac{e^{-\beta H_0}}{Z_0} \tag{2.6}$$

$$= \frac{1}{Z_0} \sum_n e^{-\beta E_n^0} \left| E_n^0 \right\rangle \left\langle E_n^0 \right|, \tag{2.7}$$

where we have used the definition of the partition function, $Z_0 = Tr(e^{-\beta H_0})$, and the spectral decomposition of H_0, given by $H_0 = \sum_n E_n^0 \left| E_n^0 \right\rangle \left\langle E_n^0 \right|$.

Step 2: Energy measurement in the basis of the current Hamiltonian, which is H_0. To calculate the probability of obtaining the result E_n^0, we use the general rule for probabilities in terms of the density operator [27], namely,

$$p_n^0 = Tr(\rho_0^{th} \left| E_n^0 \right\rangle \left\langle E_0^n \right|) = \frac{e^{-\beta E_0^n}}{Z_0}, \tag{2.8}$$

which is the usual probability of excitation of a thermal state.

After this measurement the system collapses to the energy eigenstate associated with the measured energy, which is $\left| E_n^0 \right\rangle$ in this case. If the state before the measurement were in a superposition of different energy eigenstates, or equivalently, if there were any *coherences* in the basis of H_0, the information about this superposition would be lost in the measurement. This can be considered a limitation of this definition since coherence is an important resource of quantum systems.

Step 3: Apply some force protocol that changes the Hamiltonian $H(t) \equiv H(\lambda(t))$ via some set of external parameters, represented by $\lambda(t)$, from the initial Hamiltonian $H(t_0) \equiv H_0$ to the final one $H(\tau) \equiv H_\tau$. For this protocol, the resulting time-evolution operator, as described in the last chapter, is $U(\tau, t_0) \equiv U_\tau$. The system, that is in the collapsed state $\left| E_n^0 \right\rangle$, evolves to $U_\tau \left| E_n^0 \right\rangle$.

Step 4: Perform a second energy measurement in the basis of the instantaneous Hamiltonian, which is now H_τ.

The probability to obtain the energy E_m^τ given that we measured E_n^0 in the first measurement is given by the Born rule:

$$p_{m|n} = \left| \langle E_m^\tau | U_\tau \left| E_n^0 \right\rangle \right|^2. \tag{2.9}$$

This quantity can be interpreted as the transition probability associated with the specific quantum trajectory $n \to m$. The joint probability of getting E_n^0 in the first measurement and E_m^τ in the second is given by the Bayes rule

$$p_{n,m} = p_n^0 \, p_{m|n} = \frac{e^{-\beta E_n^0}}{Z_0} \left| \langle E_m^\tau | U_\tau \left| E_n^0 \right\rangle \right|^2. \tag{2.10}$$

The quantities calculated so far are sufficient to construct the work probability distribution.

Now comes a crucial point. For the evolution described in step 3 to be inherently unitary, we must demand that the system remains isolated from any environment throughout the evolution. This means that the definition of work presented here is valid only for processes in which only work is performed on the system, while the heat exchanges with the bath are absent. This kind of dynamics resembles the adiabatic processes in the context of thermodynamics, that are processes that occur with no heat exchange. For a work protocol done on an isolated system, the work is the only energy exchange present, and therefore we can safely associate any variation in the energy of the system to the work performed by the agent that varies the parameters of the Hamiltonian. We therefore define the work of the specific trial associated with the trajectory $n \to m$ as

$$W_{m,n} = E_m^\tau - E_n^0. \tag{2.11}$$

For a system with a finite number of energy levels, the work on each trial is also discrete and has one value for each possible transition between energy levels. To obtain a continuous probability distribution, such as in equation 2.3, we use a sum of

delta functions centered at each possible transition. We then have

$$P(W) = \sum_{m,n} \delta(W - W_{m,n}) \, p_{m,n} \tag{2.12}$$

$$= \sum_{m,n} \delta(W - (E_m^\tau - E_n^0)) \frac{e^{-\beta E_n^0}}{Z_0} \left| \langle E_m^\tau | U_\tau | E_n^0 \rangle \right|^2.$$

The average work can then be computed using equation 2.1. We have

$$\langle W \rangle = \int dW \, P(W) \, W$$

$$= \sum_{m,n} p_{m,n} \int dW \, \delta(W - W_{m,n}) \, W \tag{2.13}$$

$$= \sum_{m,n} p_{m,n} \, W_{m,n}.$$

As expected, the delta functions transform the integral into a discrete sum, and we can see that the work is quantized as a consequence of the discreteness of the energy levels. We can further simplify this expression using equations (2.10) and (2.11), as

$$\langle W \rangle = \sum_{m,n} \frac{e^{-\beta E_0^n}}{Z_0} \langle E_m^\tau | U_\tau | E_n^0 \rangle \langle E_n^0 | U_\tau^\dagger | E_m^\tau \rangle \, (E_m^\tau - E_n^0).$$

$$= \sum_{m,n} \frac{e^{-\beta E_0^n}}{Z_0} E_m^\tau \langle E_m^\tau | U_\tau | E_n^0 \rangle \langle E_n^0 | U_\tau^\dagger | E_m^\tau \rangle$$

$$- \sum_{m,n} \frac{e^{-\beta E_0^n}}{Z_0} E_n^0 \langle E_m^\tau | U_\tau | E_n^0 \rangle \langle E_n^0 | U_\tau^\dagger | E_m^\tau \rangle. \tag{2.14}$$

We treat each term in the right hand side of the expression above separately. For the first, we rearrange the factors to obtain

$$\sum_m \langle E_m^\tau | U_\tau \left(\sum_n \frac{e^{-\beta E_n^0}}{Z_0} | E_n^0 \rangle \langle E_n^0 | \right) U_\tau^\dagger E_m^\tau | E_m^\tau \rangle = \sum_m \langle E_m^\tau | (U_\tau \rho_0^{th} U_\tau^\dagger) H_\tau | E_m^\tau \rangle$$

$$\tag{2.15}$$

$$= Tr(\rho_\tau \, H_\tau),$$

where we have used the expression for the initial thermal state ρ_0^{th} in (2.7) and the eigenvalue equation $E_m^\tau | E_m^\tau \rangle = H_\tau | E_m^\tau \rangle$. We have also defined $\rho_\tau \equiv U_\tau \rho_0^{th} U_\tau^\dagger$, that is the initial thermal state evolved through the time evolution operator associated with the work protocol, which will be a non-equilibrium state if the process is not

q-adiabatic. In the two-point measurement protocol, recall that the time evolution operator acts on the energy eigenstate associated with the outcome of the measurement $|E_n^0\rangle$ and not on the initial state ρ_0^{th}. Nonetheless, the state $U_\tau \rho_0^{th} U_\tau^\dagger$ appears in the expression for the average work, which is an interesting fact.

For the second term in (2.14), we identify the expression of ρ_0^{th} as well, and we again use $E_n^0 |E_n^0\rangle = H_0 |E_n^0\rangle$ to substitute the initial Hamiltonian in the expression. We also arrange the other factors to obtain

$$\sum_m (\langle E_m^\tau | U_\tau) \left(\sum_n \frac{e^{-\beta E_n^0}}{Z_0} E_n^0 |E_n^0\rangle \langle E_n^0| \right) (U_\tau^\dagger |E_m^\tau\rangle) = \sum_m \langle E_m^0| \rho_0^{th} H_0 |E_m^0\rangle$$
$$= Tr(\rho_0^{th} H_0), \tag{2.16}$$

since the time evolution operator U_τ is associated with the change in the Hamiltonian $H_0 \to H_\tau$, then it also associates the eigenstates of these two Hamiltonians by the equation $|E_m^\tau\rangle = U_\tau |E_m^0\rangle$. Since U_τ is unitary, we also have $U_\tau^\dagger |E_m^\tau\rangle = |E_m^0\rangle$, which was used in the first step of the derivation above. Substituting the terms in equation (2.14) the average work becomes

$$\langle W \rangle = Tr(\rho_\tau H_\tau) - Tr(\rho_0^{th} H_0) = \langle H_\tau \rangle - \langle H_0 \rangle. \tag{2.17}$$

An important aspect of the definition of work presented above is that it is possible to formulate fluctuation theorems analogous to Jarzynski's equality in this context if the system's initial state is given by a Gibbs state. The derivation for these quantum fluctuation theorems can be found, for example, in [26]. Note that the right-hand side of equation (2.17) is equivalent to the difference in the expectation value of the Hamiltonian at the begging and the end of the work protocol if no energy measurements were made at all, however, this only works if the initial density operator before the measurement is diagonal in the basis of the initial Hamiltonian, and for this reason this definition of work does not account for initial coherence of the working substance [28].

2.4   Heat exchange in a thermalization process

It is also possible to formulate a quantum definition for the heat exchanged in the thermalization of a quantum system coupled to a thermal bath. In the same way as

the definition of work above, here we assume that there are no other energy exchanges along the thermalization, and therefore we can associate all energy variations to the heat flow. No work is, thus, applied to the system in this scenario.

Step 1: Prepare the system in a non-equilibrium state ρ_τ at the instant $t = \tau$. In the context we are interested, this state is usually the result of some irreversible work protocol applied over an initial thermal state, like $U_\tau \rho_0^{th} U_\tau^\dagger$. Even if the system is in a non-equilibrium state, it still has some instantaneous Hamiltonian, that we define as H_τ.

Step 2: Projective energy measurement in the instantaneous Hamiltonian basis, which is $\{|E_n^\tau\rangle\}$. The probability to obtain the energy E_n^τ as outcome is

$$p_n^\tau = Tr(\rho_\tau |E_n^\tau\rangle \langle E_n^\tau|) \tag{2.18}$$

$$= \langle E_n^\tau| \rho_\tau |E_n^\tau\rangle . \tag{2.19}$$

After this measurement the state becomes $|E_n^\tau\rangle$.

Step 3: Put the system in contact with a thermal reservoir at inverse temperature $\beta = 1/k_b T$. Using the assumption of thermalization and not assuming any details of the bath structure, for generality, the state of the system at the end of this process is given by

$$\rho_\tau^{th} = \frac{e^{-\beta H_\tau}}{Z_\tau}, \tag{2.20}$$

where $Z_\tau = \mathrm{Tr}(e^{-\beta H_\tau})$. Note that since no work has been applied to the system during the thermalization, the Hamiltonian remains the same.

Step 4: We then measure the energy a second time. Since the Hamiltonian did not change, we make this measurements again in the basis of H_τ. Like before, we wish to compute the probability to measure a different outcome E_m^τ given that we obtained E_n^τ in the first measurement. However, this time the final equilibrium state ρ_τ^{th} carries no information about the initial non-equilibrium state ρ_τ, as it happens in any complete thermalization process. Because of this, the conditional probability $p_{m|n}$ of measuring E_m^τ given that we measured E_n^τ in step 2 will not dependent on the result of the first measurement, and therefore it will not carry an index n. This probability is, therefore, trivially found to be the thermal occupation probability given by the

Boltzmann distribution, namely,

$$p_{m|n} = p_m = \frac{e^{-\beta E_m^\tau}}{Z_\tau}, \tag{2.21}$$

and the joint probability to measure E_n^τ and then E_m^τ is

$$p_{m,n} = p_n^\tau \, p_{m|n} = \langle E_n^\tau | \, \rho_\tau \, | E_n^\tau \rangle \frac{e^{-\beta E_m^\tau}}{Z_\tau}. \tag{2.22}$$

Again, since the system exchanges energy exclusively with the bath, we define the heat of a specific trajectory $n \to m$ as the difference between the two values of the energy measurements.

$$Q_{m,n} = E_m^\tau - E_n^\tau. \tag{2.23}$$

As we have done for the work in equation (2.12), we define a probability distribution for the exchanged heat, $P(Q)$, given by

$$
\begin{aligned}
P(Q) &= \sum_{m,n} \delta(Q - Q_{m,n}) p_{m,n} \\
&= \sum_{m,n} \delta(Q - Q_{m,n}) \langle E_m^\tau | \, \rho_\tau \, | E_m^\tau \rangle \frac{e^{-\beta E_m^\tau}}{Z_\tau},
\end{aligned} \tag{2.24}
$$

and the average heat is given by

$$\langle Q \rangle = \sum_{m,n} p_{m,n} \, Q_{m,n} \tag{2.25}$$

$$= \sum_n \langle E_n^\tau | \, \rho_\tau \, | E_n^\tau \rangle \sum_m \frac{e^{-\beta E_m^\tau}}{Z_\tau} E_m^\tau - \sum_n \langle E_n^\tau | \, \rho_\tau \, H_\tau \, | E_n^\tau \rangle \sum_m \frac{e^{-\beta E_m^\tau}}{Z_\tau} \tag{2.26}$$

$$= Tr(\rho_\tau^{th} \, H_\tau) - Tr(\rho_\tau \, H_\tau). \tag{2.27}$$

The first summation in the second step of the derivation above is unity because of the unity of the trace of density operators. The second one is just a sum of the energy eigenvalues of H_τ weighted by the probabilities of occupation of a thermal state, which is just the average energy $\langle H_\tau \rangle = Tr(\rho_\tau^{th} H_\tau)$. In the third summation, we have used again the eigenvalue equation $E_n^\tau | E_n^\tau \rangle = H_\tau | E_n^\tau \rangle$. For the last summation, note that it contains a sum of all Boltzmann weights (probabilities), that are unity as well.

Notice that in the definitions of heat and work we assumed that only one type of energy exchange happens at a time. However, it is possible to formulate a two-point

measurement scenario to define heat and work when the working substance is weakly coupled to a thermal bath, as it is described in [29].

With the expressions for the average work and average heat in t-adiabatic and pure thermalization processes, we can proceed with our analysis of quantum heat engines.

Chapter 3

Heat and work of a single spin $1/2$ thermal machine

One of the goals in the field of quantum thermodynamics is to understand what advantages can be obtained by using quantum systems as the working substance of thermal machines. In this chapter we study the quantum Otto cycle for a single spin $1/2$ system in a review based on the work in [1]. Here our objective is to describe the formalism used to compute the relevant thermodynamic quantities of the machine, which are the work performed and the heats exchanged with the thermal reservoirs.

3.1 The working substance

Every physical system with spin has also a magnetic moment associated to it given by the equation $\vec{\mu} = g_m \vec{S}$, where g_m is the gyromagnetic factor that depends on the nature of the spin system analyzed. For spin $1/2$ systems, the spin vector is composed by the Pauli operators in the expression $\vec{S} = \frac{\hbar}{2}(\sigma_x, \sigma_y, \sigma_z)$.

Consider a situation where a spin $1/2$ system interacts with some time-dependent and externally driven magnetic field $\vec{B}(t)$. There will be a potential energy associated to this interaction, and from this energy we can construct the Hamiltonian for this system, given by

$$H(t) = -\vec{\mu} \cdot \vec{B}(t) \tag{3.1}$$

$$= x(t)\sigma_x + y(t)\sigma_y + z(t)\sigma_z, \tag{3.2}$$

where we defined the vector $(x(t), y(t), z(t)) \equiv -\frac{\hbar}{2}g_m(B_x(t), B_y(t), B_z(t))$. The most

relevant aspect here is that this vector holds all the information regarding the magnetic field that drives the working substance.

The energy eigenvalues or the spacing between the two energy levels are associated with the intensity of the magnetic field. For a given time instant t the level spacing $\omega(t)$ is given by [1]

$$\hbar\omega(t) = 2\sqrt{x^2(t) + y^2(t) + z^2(t)}. \tag{3.3}$$

This quantity is also known in the literature [7] as the Rabi frequency.

As we have seen in chapter 2, the time evolution operator (TEO) for a time-dependent system can be straightforwardly calculated if the Hamiltonian is a linear combination of generators of the su(2), su(1,1) or su(2,1) Lie algebras. Fortunately, it is a well know fact that the Pauli operators in (3.2) obey the commutation relations of the su(2) Lie algebra, and therefore we can apply the method described in 1.4 to obtain the TEO for this system.

We first rewrite the Hamitlonian in terms of σ_z and the ladder operators, defined as

$$\sigma_\pm = \frac{\sigma_x \pm i\sigma_y}{2}, \tag{3.4}$$

which can be inverted to obtain

$$\sigma_x = \sigma_+ + \sigma_-, \qquad\qquad \sigma_y = \frac{\sigma_+ - \sigma_-}{i}. \tag{3.5}$$

The matrix representation of these operators in the basis of σ_z is

$$\sigma_+ = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}, \qquad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \qquad \sigma_- = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}. \tag{3.6}$$

The commutation relations between these operators can be easily verified to be

$$[\sigma_-, \sigma_+] = -\sigma_z, \qquad\qquad [\sigma_z, \sigma_\pm] = \pm 2\sigma_\pm. \tag{3.7}$$

To make the association with the TEO found in 1.4 we define $T_c \equiv \sigma_z/2$ and $T_\pm \equiv \sigma_\pm$. The commutation relations above become

$$[T_-, T_+] = -2T_c, \qquad\qquad [T_c, T_\pm] = \pm T_\pm, \tag{3.8}$$

which are the commutation relations for the su(2) Lie algebra, as presented in (1.17) ($\delta = -1$, $\epsilon = 1$). The Hamiltonian in 3.2 in terms of these operators becomes

$$H(t) = \eta_+(t)T_+ + \eta_c(t)T_c + \eta_-(t)T_-, \tag{3.9}$$

with

$$\eta_\pm(t) = x(t) \mp iy(t) \qquad \text{and} \qquad \eta_c(t) = 2z(t). \tag{3.10}$$

The time evolution operator for a given trajectory of the magnetic field between two instants t_1 and t_2 will then be given by

$$U(t_2, t_1) = e^{\alpha_N T_+} e^{\ln(\beta_N) T_c} e^{\gamma_N T_-} \tag{3.11}$$

$$= e^{\alpha_N \sigma_+} e^{\ln \sqrt{\beta_N} \sigma_z} e^{\gamma_N \sigma_-}, \tag{3.12}$$

where the coefficients $(\alpha_N, \beta_N, \gamma_N)$ are given by the equations in (1.30). We can rewrite the operator above in matrix form. First, consider the easily verifiable fact that $\sigma_\pm^2 = 0$, which leads to $e^{x\sigma_\pm} = \mathbb{1} + x\,\sigma_\pm$. The term $e^{\ln \sqrt{\beta_N} \sigma_z}$ can be straightforwardly calculated in the basis of σ_z. We then have, after some algebra,

$$e^{\ln \sqrt{\beta_N} \sigma_z} = \begin{bmatrix} \sqrt{\beta_N} & 0 \\ 0 & -\frac{1}{\sqrt{\beta_N}} \end{bmatrix}, \quad e^{\alpha_N \sigma_+} = \begin{bmatrix} 1 & \alpha_N \\ 0 & 1 \end{bmatrix}, \quad e^{\gamma_N \sigma_-} = \begin{bmatrix} 1 & 0 \\ \gamma_N & 1 \end{bmatrix}. \tag{3.13}$$

The time evolution operator is just the product of the expressions above

$$U(t_2, t_1) \equiv U_\tau = \frac{1}{\sqrt{\beta_N}} \begin{bmatrix} \beta_N + \alpha_N \gamma_N & \alpha_N \\ \gamma_N & 1 \end{bmatrix}. \tag{3.14}$$

With the $(\alpha_N, \beta_N, \gamma_N)$ coefficients calculated numerically, we obtain all the information about the dynamics of the system subject to the Hamiltonian in (3.2), given some initial state.

Now we consider the same scenario of 2.3, where some general trajectory of the magnetic field $(x(t), y(t), z(t))$, or *sweep*, changes the Hamiltonian from an initial one $H(t_1) \equiv H_1$ to a final one $H(t_2) \equiv H_2$. The initial and final energy level spacings are given in (3.3), with $\omega(t_1) \equiv \omega_1$ and $\omega(t_2) \equiv \omega_2$. The energy eigenvalues and eigenstates at the instants t_1 and t_2 are given by

$$H_r \left| E_m^{(r)} \right\rangle = E_m^{(r)} \left| E_m^{(r)} \right\rangle, \quad m, r = 1, 2. \tag{3.15}$$

The index m covers the different energy eigenstates, and r is associated with the two time instants. If we define $m = 1$ for the groundstate, the eigenvalues will be given by $E_1^{(r)} = -\frac{\hbar\omega_r}{2}$ and $E_2^{(r)} = +\frac{\hbar\omega_r}{2}$. Another important quantity to compute is the transition probability matrix between instantaneous energy eigenstates, that has already appeared in the two-point measurement scheme in the last chapter (2.9), namely,

$$p_{i|j} = \left| \left\langle E_i^{(2)} \middle| U_\tau \middle| E_j^{(1)} \right\rangle \right|^2. \tag{3.16}$$

It can be seen that $p_{i|j}$ is a symmetric matrix ($p_{i|j} = p_{j|i}$) with real entries between $[0, 1]$ since they are probabilities. There is a property of this matrix that is of key importance, it is *doubly stochastic* [1], which means

$$\sum_j p_{i|j} = \sum_i p_{i|j} = 1, \tag{3.17}$$

which follows from

$$\sum_j p_{i|j} = \sum_j \left\langle E_i^{(2)} \middle| U_\tau \middle| E_j^{(1)} \right\rangle \left\langle E_j^{(1)} \middle| U_\tau^\dagger \middle| E_i^{(2)} \right\rangle \tag{3.18}$$

$$= \left\langle E_i^{(2)} \middle| U_\tau U_\tau^\dagger \middle| E_i^{(2)} \right\rangle = 1, \tag{3.19}$$

and the same goes for the summation in the index i. This property is a consequence of the completeness of the basis of energy eigenstates, $\sum_j \left| E_j^{(r)} \right\rangle \left\langle E_j^{(r)} \right| = \mathbb{1}$, and from the unitarity of the time evolution operator, $U_\tau U_\tau^\dagger = \mathbb{1}$.

For the case of a single q-bit, the matrix $p_{i|j}$ is 2×2. For a symmetric and doubly stochastic 2×2 matrix it is possible to write all the 4 matrix elements in terms of only one. More specifically, if we make $p_{1|1} = P$ the matrix becomes

$$\begin{bmatrix} p_{1|1} & p_{1|2} \\ p_{2|1} & p_{2|2} \end{bmatrix} = \begin{bmatrix} P & 1-P \\ 1-P & P \end{bmatrix}. \tag{3.20}$$

The parameter P can be interpreted as the probability of permanence in the ground state after the sweep of the magnetic field has been made. It is a convenient definition, since it carries all the information about the specific trajectory of the magnetic field and lets us treat the problem in a general form, *i.e.*, independent of the procotol. In particular, this parameter gives us direct information on how close the protocol is to the adiabatic limit. Since there can be no transitions between instantaneous

eigenstates in an adiabatic process, the probability of permanence must be 1 in this limit. We then have that $P \to 1$ as we perform more slower sweeps.

With the energy eigenvalues given in (3.15) and the P parameter calculated by the algebraic method presented in 1.4 we can compute all the relevant quantities needed for the analysis of the thermal machine, which is the topic of the next section.

3.2 Single q-bit Otto Cycle

The Otto cycle is a four-stroke protocol. In two of the strokes, work is applied in the absence of heat exchanges with thermal reservoirs. In the context of classical thermodynamics, processes which occur in thermal isolation are called adiabatic, and it is important to differentiate these processes from the quantum adiabatic processes described in section 1.1.3. To avoid confusion we shall name t-adiabatic the thermodynamic adiabatic processes and q-adiabatic the ones in the quantum regime. Using this terminology, two of the strokes of the Otto Cycle are t-adiabatic but are not necessarily q-adiabatic. In general the work strokes in the classical Otto cycle are assumed to be quasi-static, which would make them q-adiabatic as well in this context.However, here we wish to explore the consequences of driving the working substance away from equilibrium, and therefore we also consider protocols that are not q-adiabatic. The pure quantum work strokes are described by the methods discussed in the last section and in 2.3.

In the other two strokes, which we call thermalization strokes, no work is performed on the working substance as it is left to reach equilibrium with a thermal bath. We consider the case where the cycle operates between two temperatures T_h and T_c, with $T_h > T_c$. This protocol is analogous to the one described in 2.4. As shown in (2.27), the average heat exchanged in these strokes is the difference between the energy expectation values at the beginning and end of the thermalization protocols. As will be shown, the heats exchanged in the thermalization strokes are sufficient to compute the other relevant quantities like work and efficiency.

To illustrate the cycle of the machine, we consider that the working substance is transformed between four states denoted by (A, B, C, D), and the strokes link them. In the following, we compute the density operator and the average energy at all four

points.

Point A: The system is initially prepared at thermal equilibrium with the hot reservoir with some initial Hamiltonian H_1. As described in equation 3.15, the eigenvalues of H_1 are associated to the frequency ω_1. The density operator ρ_A will then be diagonal in the basis of H_1. We have, after a straightforward calculation,

$$\rho_A = \frac{e^{-\beta_h H_1}}{Z_1} = \frac{1}{2\cosh\left(\beta_h \frac{\hbar\omega_1}{2}\right)} \begin{bmatrix} e^{-\beta_h \frac{\hbar\omega_1}{2}} & 0 \\ 0 & e^{\beta_h \frac{\hbar\omega_1}{2}} \end{bmatrix}, \qquad (3.21)$$

with the partition function given by $Z_1 = Tr(e^{-\beta_h H_1})$. The average energy is then given by

$$E_A = \mathrm{Tr}(\rho_A H_1) = \frac{\left(\frac{\hbar\omega_1}{2}\right)}{2\cosh\beta_1\frac{\hbar\omega_1}{2}} \mathrm{Tr}\begin{bmatrix} e^{-\beta_h \frac{\hbar\omega_1}{2}} & 0 \\ 0 & -e^{\beta_h \frac{\hbar\omega_1}{2}} \end{bmatrix} \qquad (3.22)$$

$$= -\frac{\hbar\omega_1}{2} \tanh\left(\beta_h \frac{\hbar\omega_1}{2}\right), \qquad (3.23)$$

which is the usual expression for the mean energy of a spin $1/2$ system in a thermal state.

Point B: The stroke $A \to B$ is t-adiabatic, therefore work is applied to the system while no heat is exchanged. The Hamiltonian varies from H_1 to H_2, and the resulting state is found by acting the time evolution operator on the initial thermal state, $\rho_B = U_\tau \rho_A U_\tau^\dagger$, which is a non-equilibrium state if the driving is not q-adiabatic. We can compute the average energy in terms of the elements of the transition probability matrix $p_{i|j}$ mentioned in the last section. Using the spectral decomposition of the two Hamiltonians and taking the trace in the basis of H_2 we obtain

$$\begin{aligned} E_B &= \mathrm{Tr}(\rho_B H_2) \\ &= \frac{1}{Z_1}\sum_{i,j} e^{-\beta_h E_j^{(1)}} E_i^{(2)} \mathrm{Tr}\left(U_\tau \left|E_j^{(1)}\right\rangle\left\langle E_j^{(1)}\right| U_\tau^\dagger \left|E_i^{(2)}\right\rangle\left\langle E_i^{(2)}\right|\right) \\ &= \frac{1}{Z_1}\sum_{i,j,k} e^{-\beta_h E_j^{(1)}} E_i^{(2)} \left\langle E_k^{(2)}\right| U_\tau \left|E_j^{(1)}\right\rangle\left\langle E_j^{(1)}\right| U_\tau^\dagger \left|E_k^{(2)}\right\rangle \cdot \left\langle E_j^{(2)}\middle| E_k^{(2)}\right\rangle \\ &= \frac{1}{Z_1}\sum_{i,j} e^{-\beta_h E_j^{(1)}} E_i^{(2)} \left|\left\langle E_i^{(2)}\right| U_\tau \left|E_j^{(1)}\right\rangle\right|^2. \end{aligned} \qquad (3.24)$$

We identify the last term in the above equation as the transition probability matrix between the instantaneous eigenstates of H_1 and H_2, which is given in terms of the

adiabatic parameter P, as we have seen in (3.20). Substituting the entries of this matrix, together with the values of the partition function and the energy eigenvalues, we get

$$E_B = \frac{\hbar\omega_2}{2} \tanh\left(\beta_h \frac{\hbar\omega_1}{2}\right)(1 - 2P). \tag{3.25}$$

It is easy to verify that in the adiabatic limit ($P \to 1$) we have $E_B \to E_A(\omega_2/\omega_1)$ [1], which is a common result for driven systems in the adiabatic regime.

Point C: Now the system is left to thermalize with another heat reservoir at a lower temperature $T_c = 1/k_b\beta_c$, with $\beta_h < \beta_c$. The Hamiltonian is kept constant in H_2. At the end of the protocol the state and average energy are, respectively,

$$\rho_C = \frac{e^{-\beta_c H_2}}{Z_2} = \frac{1}{2\cosh\left(\beta_c \frac{\hbar\omega_2}{2}\right)} \begin{bmatrix} e^{-\beta_c \frac{\hbar\omega_2}{2}} & 0 \\ 0 & e^{\beta_c \frac{\hbar\omega_2}{2}} \end{bmatrix}, \tag{3.26}$$

$$E_C = \text{Tr}(\rho_c H_2) = -\frac{\hbar\omega_2}{2}\tanh\left(\beta_c \frac{\hbar\omega_2}{2}\right). \tag{3.27}$$

As described in 2.4, the heat exchanged in this kind of process is just the difference between the energy averages. We introduce Q_c, the heat exchanged with the cold source, as

$$Q_c = E_C - E_B \tag{3.28}$$

$$= -\frac{\hbar\omega_2}{2}\left[\tanh\left(\frac{\beta_c\hbar\omega_2}{2}\right) + \tanh\left(\frac{\beta_h\hbar\omega_1}{2}\right)(1 - 2P)\right]. \tag{3.29}$$

Point D: The stroke $C \to D$ is another t-adiabatic stage, where the second work protocol is performed. This time the Hamiltonian changes from H_2 to H_1. It is convenient to consider that this protocol is the *time-reversed* [14] [1], or the backward protocol of the stroke $B \to C$, as such a symmetry allows to describe this protocol in terms of the TEO of the first work stroke. If the Hamiltonian has the property $KH(t)K^\dagger = H(t)$ for some antiunitary operator K and all t, then the TEO of the backward protocol is

$$\tilde{U}_\tau = KU_\tau^\dagger K^\dagger. \tag{3.30}$$

As stated in [1], the Hamiltonian in (3.2) satisfies the condition mentioned above, therefore we can use this operator in this context. This property is useful when

calculating the transition probability matrix for the backward protocol, which is

$$\left|\left\langle E_i^{(1)}\middle|\tilde{U}_\tau\middle|E_j^{(2)}\right\rangle\right|^2 = \left|\left\langle E_i^{(1)}\middle|KU_\tau^\dagger K^\dagger\middle|E_j^{(2)}\right\rangle\right|^2 \tag{3.31}$$

$$= \left|\left\langle E_i^{(1)}\middle|U_\tau^\dagger\middle|E_j^{(2)}\right\rangle^*\right|^2$$

$$= \left|\left\langle E_i^{(2)}\middle|U_\tau\middle|E_j^{(1)}\right\rangle\right|^2 = p_{j|i} = p_{i|j}.$$

The transition matrix is, therefore, the same for the time reversed protocol.

The state of the system at the end of the protocol will be another non-equilibrium state, given by $\rho_D = \tilde{U}_\tau\rho_C\tilde{U}_\tau^\dagger$. The average energy is, analogously to E_B,

$$E_D = \frac{1}{Z_2}\sum_{i,j} e^{-\beta_c E_j^{(2)}} E_i^{(1)}\left|\left\langle E_i^{(1)}\middle|\tilde{U}_\tau\middle|E_j^{(2)}\right\rangle\right|^2 \tag{3.32}$$

$$= \frac{\hbar\omega_1}{2}\tanh\left(\frac{\beta_c\hbar\omega_2}{2}\right)(1-2P), \tag{3.33}$$

which is identical to E_B if we make $\omega_1 \Leftrightarrow \omega_2$ and $\beta_c \Leftrightarrow \beta_h$. This is a consequence of choosing the backward protocol for the second work stroke.

In the last step of the cycle, the system is left to thermalize with the hot source, therefore the working substance returns to its initial state ρ_A with energy E_A. The heat exchanged in this step is given by

$$Q_h = E_A - E_D \tag{3.34}$$

$$= -\frac{\hbar\omega_1}{2}\left[\tanh\left(\frac{\beta_h\hbar\omega_1}{2}\right) + \tanh\left(\frac{\beta_c\hbar\omega_2}{2}\right)(1-2P)\right]. \tag{3.35}$$

We can use the the first law of thermodynamics for thermal machines to compute the total work delivered to the working substance in the whole cycle, namely,

$$W = Q_h + Q_c \tag{3.36}$$

$$= -\frac{\hbar}{2}\tanh\left(\frac{\beta_h\hbar\omega_1}{2}\right)[\omega_1 + \omega_2(1-2P)] - \frac{\hbar}{2}\tanh\left(\frac{\beta_c\hbar\omega_2}{2}\right)[\omega_1(1-2P) + \omega_2]. \tag{3.37}$$

3.3 Operation modes of the machine

In addition to the conservation of energy presented above, the engine must obey the constraint imposed by the Clausius inequality, $(\beta_h Q_h + \beta_c Q_c \le 0)$, which is a

consequence of the second law, as discussed in [1]. In this reference there is also a derivation showing that only four configurations of the signs of the exchanged energies (Q_h, Q_c, W) are compatible with the first and second laws and the aforementioned condition $\beta_h < \beta_c$. In our convention, $Q_{h/c} > 0$ when heat is extracted from the hot/cold sources and $W > 0$ when work is extracted from the working substance.

The four possible operation regions are illustrated in figure 3.1.
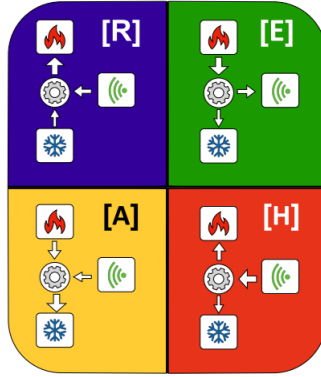

Figure 3.1: Four operation modes of a thermal machine operating between two heat reservoirs. Taken from [1].

Heater (H): In this operation mode the objective is to increase the temperature of the cold source. For this purpose, work is invested to make the heat flow to the cold source, but some part of the work is dissipated and goes to the hot source. The two heat sources receive heat, while work is invested in the working substance, therefore by the sign convention adopted we have

$$Q_h \leq 0, \quad Q_c \leq 0, \quad W \leq 0. \tag{3.38}$$

Thermal Accelerator (A): Here, work is again invested, but this time to extract heat from the hot source and take it to the cold one. Since this process would happen spontaneously, the work applied makes it happen faster. Now heat is extracted from the hot source, therfore we have

$$Q_h \geq 0, \quad Q_c \leq 0, \quad W \leq 0. \tag{3.39}$$

Refrigerator (R): Here the objective is to extract heat from the cold source to decrease even more its temperature. We invest work to make the heat flow from the

hot source to the cold one. We can see that, in this case, the hot source receives heat, the cold source loses heat, and the working substance receives work. Therefore, we have

$$Q_h \leq 0, \quad Q_c \geq 0, \quad W \leq 0. \tag{3.40}$$

Engine (E): This is the only mode of operation allowed where work is extracted from the working substance. This operation mode consists of extracting heat from the hot source and convert some part of this heat into work. The amount of heat that cannot be harnessed as work gets dissipated to the cold source. The conditions are, therefore,

$$Q_h \geq 0, \quad Q_c \leq 0, \quad W \geq 0. \tag{3.41}$$

In [1] an analysis is made to investigate which set of parameters of the engine $(\omega_1, \omega_2, \beta_1, \beta_2, P)$ gives rise to different operation modes, as well as other interesting discussions. However, since we already introduced the machine cycle and the procedures to compute the heats and work, we proceed to the main discussion: the machine consisting of two interacting spins $1/2$.

Chapter 4

Two q-bit engine with isotropic interaction

In this chapter we use the framework described so far to analyze an Otto cycle with a working substance composed of two interacting spins, or q-bits. The spins are driven by a global interaction with a time-dependent external magnetic field that can vary in direction and intensity. We also consider an interaction between the two q-bits analogous to the one in the Heisenberg XXX (or isotropic) Hamiltonian for two spins [30]. An Otto cycle with this interaction model was presented in [6, 12], but they consider the magnetic field fixed in one direction, which causes the Hamiltonian to commute at different times.

The discussion goes as follows: We start by describing the working substance for arbitrary protocols, and we make considerations regarding the operation regions of the machine and the coupling effects on them. Next, we investigate the effects of nonadiabaticity in the operation of the machine while considering a specific trajectory of the magnetic field.

4.1   The working substance

Since we are dealing with a system of interacting spins, the total Hamiltonian of the working substance will be composed of a term associated with the external driving of the magnetic field as well as an internal term, related to the coupling. We discuss the properties of these two terms, and also present the method used to compute the time evolution operator for this system.

4.1.1   The external Hamiltonian

We consider an external magnetic field that couples to the total magnetic moment of the two spins. This magnetic moment is proportional to the the global angular momentum operator: $\vec{S} = \vec{S}_1 + \vec{S}_2$, and the magnetic moment is $\vec{\mu} = g_m \vec{S}$. As described by the usual rules of addition of angular momenta [15], the Hilbert space of the total angular momentum operator of this system can be divided into two separate subspaces. The first, which is called the *singlet*, is one-dimensional, and the states in it have zero angular momentum ($S = 0$). The *triplet* is three-dimensional, and is associated with $S = 1$. Because of this property, all three components of the total angular momentum operator $\vec{S} = (S_x, S_y, S_z)$ are block diagonal in the singlet and triplet subspaces. These operators are defined in terms of the individual angular momenta by

$$S_i = \frac{\hbar}{2}\left(\sigma_{i1} \otimes \mathbb{1}_2 + \mathbb{1}_1 \otimes \sigma_{i2}\right) \equiv \frac{\hbar}{2}(\sigma_1^i + \sigma_2^i), \tag{4.1}$$

where σ_{ik} is the i-th component of the k-th spin. In our case, we have $i = x, y, z$ and $k = 1, 2$.

We call H_{ext} the part of the Hamiltonian associated to the interaction with the magnetic field. We have

$$
\begin{aligned}
H_{ext}(t) &= -\vec{\mu} \cdot \vec{B}(t) \\
&= X(t)(\sigma_1^x + \sigma_2^x) + Y(t)(\sigma_1^y + \sigma_2^y) + Z(t)(\sigma_1^z + \sigma_2^z),
\end{aligned}
\tag{4.2}
$$

where we have defined $(X(t), Y(t), Z(t)) = -g_m \frac{\hbar}{2}(B_x(t), B_y(t), B_z(t))$, analogously to what was done in 3.1. Since this Hamiltonian is a linear combination of the components of the global angular momentum, it is also block diagonal in the singlet and triplet subspaces. We can again associate a Rabi frequency to the intensity of the magnetic field, that is

$$\hbar\omega(t) = 2\sqrt{X^2(t) + Y^2(t) + Z^2(t)}. \tag{4.3}$$

With this definition the eigenvalues of the external Hamiltonian become $+\hbar\omega(t), 0$ and $-\hbar\omega(t)$, with a double degeneracy in the null eigenvalue. Since the addition of two angular momentum operators is another legitimate angular momentum, the

components of $\vec{S}$ must obey the commutation relations given by $[S_i, S_j] = i\hbar\epsilon_{ijk}S_k$. As we have seen in 3.1, these commutation relations are associated with the su(2) Lie algebra, and therefore we could use the algebraic method presented in section 1.4 to describe the dynamics of this system, if we only had $H_{ext}(t)$.

Following the procedure used for the case of a single q-bit, we define global ladder operators given by

$$\sigma_{\pm}^S = (\sigma_1^x + \sigma_2^x) \pm i(\sigma_1^y + \sigma_2^y). \tag{4.4}$$

In terms of them the Hamiltonian becomes

$$\begin{aligned} H_{ext}(t) &= \frac{(X(t) - iY(t))}{2}\sigma_+^S + Z(t)(\sigma_1^z + \sigma_2^z) + \frac{(X(t) + iY(t))}{2}\sigma_-^S \\ &= \eta_+(t)T_+ + \eta_c(t)T_c + \eta_-(t)T_-, \end{aligned} \tag{4.5}$$

with

$$\begin{aligned} \eta_{\pm}(t) &= X(t) \pm iY(t), & \eta_c(t) &= 2Z(t), \\ T_{\pm} &= \frac{\sigma_{\pm}^S}{2}, & T_c &= \frac{(\sigma_1^z + \sigma_2^z)}{2}. \end{aligned} \tag{4.6}$$

It can be straightforwardly checked that T_+, T_c and T_-, as defined above, satisfy the commutation relations of the su(2) Lie algebra in the form presented in 3.1 and 1.2. By the methods already discussed before, we conclude that the time-evolution operator generated by an arbitrary sweep of the magnetic field is of the form

$$\begin{aligned} U_{ext} &= e^{\alpha T_+} e^{\ln\beta\, T_c} e^{\gamma T_-} \\ &= \exp\left\{\alpha\frac{\sigma_+^S}{2}\right\} \exp\left\{\ln\beta\frac{(\sigma_1^z + \sigma_2^z)}{2}\right\} \exp\left\{\gamma\frac{\sigma_-^S}{2}\right\}, \end{aligned} \tag{4.7}$$

where the parameters (α, β, γ) can be calculated numerically, as described in 1.4.

4.1.2 The interaction Hamiltonian

For systems of interacting spins, there are numerous models that describe a variety of situations, and the Heisenberg model for spin lattices is a well known example, as described in [30]. Following the references [6],[9] and [10] we analyze the 1D isotropic

Heisenberg model for the interaction. The internal Hamiltonian that describes the interaction between the two q-bits is given by

$$H_{int} = J\left(\vec{\sigma_1}\cdot\vec{\sigma_2} + \vec{\sigma_2}\cdot\vec{\sigma_1}\right) - 2J \tag{4.8}$$
$$= 2J\left(\sigma_{1x}\otimes\sigma_{2x} + \sigma_{1y}\otimes\sigma_{2y} + \sigma_{1z}\otimes\sigma_{2z}\right) - 2J,$$

where J is the coupling parameter. We have subtracted a term $2J$ to shift the zero of energy and simplify the expressions of the eigenvalues of this Hamiltonian and the rest of the expressions throughout this chapter. We can do this because the zero of energy does not affect the calculated quantities, such as heat and work, since they are given by energy differences, therefore this term always cancels out. The eigenvalues of H_{int} can be easily computed, they are $\{-8J, 0, 0, 0\}$. Note that the interaction Hamiltonian is null in its degenerate subspace. The sign of the coupling parameter determines if we are in the antiferromagnetic ($J < 0$), or in the ferromagnetic ($J > 0$) regimes. We restrict ourselves to the antiferromagnetic case, which is more interesting since it is the only one that can exhibit quantum entanglement, as proven in [9]. This model is called isotropic because the coupling parameter is the same for all three directions. For this reason, even if the coupling changes in time, the internal Hamiltonian will commute with itself at different times, and therefore the time-evolution operator can be easily found, as described in 1.1.2. In this work we proceed in the case of a constant coupling parameter. We have, therefore, for a protocol occurring in a time interval $\Delta t = t_2 - t_1$,

$$U_{int} = \exp\left\{-\frac{i}{\hbar}H_{int}\Delta t\right\}. \tag{4.9}$$

For a time-dependent coupling this operator would be given by an expression analogous to (1.9), but since this Hamiltonian commutes at different times, this time-dependence would not interfere much in the behavior of the system.

There is another property of this interaction model that we would like to highlight. As described in Ref. [15], the operator $\vec{\sigma}_1\cdot\vec{\sigma}_2$ is proportional to the product of local angular momenta, $\vec{S}_1\cdot\vec{S}_2$, which can be written as

$$\vec{S}_1\cdot\vec{S}_2 = \frac{1}{2}\left(S_1^2 + S_2^2 - S^2\right)$$
$$= \frac{1}{2}\left(\frac{3\hbar^2}{2} - S^2\right). \tag{4.10}$$

For spin 1/2 systems, the square of the local angular momenta is proportional to the identity, *i.e.*, $S_i^2 = \frac{3\hbar^2}{4}\mathbb{1}$, $i = 1, 2$. We can see by the expression above that the interaction term depends only on the square of the global angular momentum operator S^2, which commutes with S_x, S_y and S_z, as can be easily verified. Since H_{ext} is a linear combination of the components of the global angular momentum, we have

$$[H_{ext}(t), H_{int}] = 0, \forall t, \tag{4.11}$$

which is a direct consequence of the isotropy of this interaction. There are interesting effects that occur when the internal and external Hamiltonians do not commute, as it is described in [31] for a different model of interacting q-bits. We have also seen that this interaction term has only one non-zero energy eigenvalue, which is another very restrictive hypothesis. The study of this system is, nonetheless, justified, since the coupling between the spins still has a significant contribution to the efficiency of the machine, as demonstrated in [6] for the adiabatic version of this model, which is a particular case of our analysis.

Accordingly, the complete Hamiltonian we consider is the sum of the external and internal parts, namely,

$$\begin{aligned} H(t) &= H_{ext}(t) + H_{int} \\ &= \frac{(X(t) - iY(t))}{2}\sigma_+^S + Z(t)(\sigma_1^z + \sigma_2^z) + \frac{(X(t) + iY(t))}{2}\sigma_-^S \\ &+ J\left(\vec{\sigma_1} \cdot \vec{\sigma_2} + \vec{\sigma_2} \cdot \vec{\sigma_1}\right) - 2J. \end{aligned} \tag{4.12}$$

The eigenvalues corresponding to the addition of any two commuting operators are given by the sum of the eigenvalues of the added operators. Since H_{ext} commutes with H_{int} and their eigenvalues are already known, we can easily obtain the eigenvalues of $H(t)$. They are

$$\begin{aligned} E_1(t) &= -8J, & E_2(t) &= \hbar\omega(t), \\ E_3(t) &= 0, & E_4(t) &= -\hbar\omega(t). \end{aligned} \tag{4.13}$$

Differently from the case of a single q-bit, the energy eigenvalues depend on the coupling constant as well as the Rabi frequency.

Another advantage of the commutation relations between the external and internal Hamiltonians in (4.11) is that we can obtain the time-evolution operator for the

complete Hamiltonian by just composing U_{ext} and U_{int}, given in (4.7) and (4.9), respectively. We have verified that this is the case considering the derivation presented in 1.3 and adding a constant term in the Hamiltonian that commutes with the other operators involved. The resulting time evolution operator is then

$$U = U_{ext}.U_{int}. \tag{4.14}$$

It is important to note that these two time-evolution operators commute as well.

4.1.3 The local and global basis

It is convenient to represent the relevant operators of this system in different bases. The first and most intuitive is the basis formed by the tensor product between the basis vectors of the individual angular momenta. In this basis, the matrix representation of the global angular momentum operators can be found by expression (4.1), using the usual of the Pauli operators in the basis of σ_{zi}. Therefore, we can find the representations of the z component of the total angular momentum operator and the global ladder operators as

$$\sigma_+^S = \begin{bmatrix} 0 & 2 & 2 & 0 \\ 0 & 0 & 0 & 2 \\ 0 & 0 & 0 & 2 \\ 0 & 0 & 0 & 2 \end{bmatrix}, \qquad \sigma_1^z + \sigma_2^z = \begin{bmatrix} 2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -2 \end{bmatrix}, \tag{4.15}$$

and σ_-^S is just the Hermitian conjugate of σ_+^S.

Using the notation from quantum information, the vectors that span this basis can be written as $\{|00\rangle, |01\rangle, |10\rangle, |11\rangle\}$, where the $|0\rangle$ and $|1\rangle$ states correspond to the fundamental and excited states for each q-bit, respectively. Since the states that compose this basis are all product states, this basis is convenient to analyze the properties of each separate spin, and for this reason we henceforth call it the *local basis*.

Another basis that will be relevant for our description is the basis of eigenvectors of the total angular momentum operator of the two q-bits. The set of commuting observables is therefore $\{S^2, S_z\}$. This basis is convenient because the operators that compose H_{ext} are proportional to the components of $\vec{S}$, which are block diagonal in this basis, and H_{int} commutes with S^2, as we have seen.

To perform the basis transformation from the local to the global basis we construct a matrix from the eigenstates of $\{S^2, S_z\}$ written in the local basis. These eigenstates are the well known singlet and triplet states, with total angular momentum 0 and $\hbar$, respectively. This matrix is given by

$$B = \begin{bmatrix} 0 & 1 & 0 & 0 \\ -\frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}. \tag{4.16}$$

As it can be noted, two of the basis vectors of the global basis are not product states. This is why this basis is adequate to deal with operators in the joint Hilbert space of the two q-bits. To obtain the representation of some operator A in the global basis given the local one, we simply do $A \to B^\dagger A B$.

Using the expressions for the operators σ_+^S, σ_-^S, $\sigma_1^z + \sigma_2^z$ and $\vec{\sigma}_1 \cdot \vec{\sigma}_2$ in the local basis and the transformation mentioned above, we obtain the representations for the Hamiltonian in (4.12) and the time evolution operator in (4.14) in the global basis, namely

$$H = \begin{bmatrix} -8J & 0 & 0 & 0 \\ 0 & 2Z(t) & \sqrt{2}(X(t) - iY(t)) & 0 \\ 0 & \sqrt{2}(X(t) + iY(t)) & 0 & \sqrt{2}(X(t) - iY(t)) \\ 0 & 0 & \sqrt{2}(X(t) + iY(t)) & 2Z(t) \end{bmatrix}, \tag{4.17}$$

$$U = \begin{bmatrix} e^{\frac{8iJ}{\hbar}\Delta t} & 0 & 0 & 0 \\ 0 & \frac{(\alpha\gamma+\beta)^2}{\beta} & \frac{\sqrt{2}\alpha(\alpha\gamma+\beta)}{\beta} & \frac{\alpha^2}{\beta} \\ 0 & \frac{\sqrt{2}\gamma(\alpha\gamma+\beta)}{\beta} & \frac{2\alpha\gamma}{\beta} + 1 & \frac{\sqrt{2}\alpha}{\beta} \\ 0 & \frac{\gamma^2}{\beta} & \frac{\sqrt{2}\gamma}{\beta} & \frac{1}{\beta} \end{bmatrix}. \tag{4.18}$$

As it can be noted in the above matrices, both the Hamiltonian and the time evolution operator are block diagonal in the global basis, which justifies its use over the local one, where the operators have more complex forms.

In this representation, it is obvious that the singlet state, the first basis vector, is an eigenstate of the Hamiltonian with eigenvalue $-8J$. Consequently, this state evolves only through a phase factor when acted by the time-evolution operator, and therefore transitions between the singlet and the other states will not occur in this model. This fact will be useful in our calculations of the next section.

For our purposes in the treatment of the mentioned thermal machine, the coefficients (α, β, γ) of the TEO will be calculated numerically by the methods presented in 1.4. However, fortunately we can proceed with the description avoiding the cumbersome expression of the TEO by using the method exemplified in section 3.1, for a single q-bit.

4.1.4 The Transition probality matrix

We consider a generic sweep of the magnetic field that takes the Hamiltonian in 4.12 from $H_1 \equiv H(t_1)$ to $H_2 \equiv H(t_2)$. The instantaneous eigenvalues and eigenstates are given by

$$H_r \left| E_m^{(r)} \right\rangle = E_m^{(r)} \left| E_m^{(r)} \right\rangle, \quad m = 1, 2, 3, 4, \ r = 1, 2, \tag{4.19}$$

with

$$
\begin{aligned}
E_1^{(r)} &= -8J, & E_2^{(r)} &= \hbar\omega_r, \\
E_3^{(r)} &= 0, & E_4^{(r)} &= -\hbar\omega_r.
\end{aligned}
\tag{4.20}
$$

We have defined $\omega_r \equiv \omega(t_r)$, with $\omega(t)$ given in (4.3). Differently from the case of a single q-bit, the energy eigenvalues depend on the coupling parameter as well as the Rabi frequency.

As we have seen in 2.3, the work probability distribution and all the relevant thermodynamic quantities can be expressed in terms of the elements of the transition probability matrix, which is a much simpler matrix than the time evolution operator U, defined in 4.18, and is given by

$$p_{i|j} = \left| \left\langle E_i^{(2)} \middle| U \middle| E_j^{(1)} \right\rangle \right|^2. \tag{4.21}$$

This matrix has the same structure than the one for the case of the single time-dependent q-bit (see 3.1), and therefore it must also be doubly stochastic, or

$$\sum_j p_{i|j} = \sum_i p_{i|j} = 1. \tag{4.22}$$

Using these properties, we can solve a simple linear system to write all the 16 entries of $p_{i|j}$ in terms of only the diagonal elements, which are the persistence probabilities

of the instantaneous eigenstates. We can simplify this further by using the fact that the time evolution operator is block-diagonal in the global basis, discussed in the end of the previous section. Since the time evolution operator does not couple the singlet to the triplet, the probability of permanence in the singlet must be unity, and we can describe the elements of $p_{i|j}$ with just three parameters $P \equiv p_{2|2}$, $P' \equiv p_{3|3}$ and $P'' \equiv p_{4|4}$. The transition matrix can therefore be written as

$$
p_{i|j} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & P & \frac{1}{2}\left(-P' + P'' - P + 1\right) & \frac{1}{2}\left(P' - P'' - P + 1\right) \\ 0 & \frac{1}{2}\left(-P' + P'' - P + 1\right) & P' & \frac{1}{2}\left(-P' - P'' + P + 1\right) \\ 0 & \frac{1}{2}\left(P' - P'' - P + 1\right) & \frac{1}{2}\left(-P' - P'' + P + 1\right) & P'' \end{bmatrix}.
\tag{4.23}
$$

The three parameters (P, P', P''), that we call henceforth as P parameters, are the persistence probabilities on the highest energy state, the zero energy state, and the ground state, respectively, without considering the singlet. These parameters contain all the information regarding the specific dynamics generated by the sweep in the magnetic field. They are convenient because they help us to measure the degree of adiabaticity of the protocol, as they all approach unity in the adiabatic limit. A similar situation happened for the case of a single q-bit, as we have seen in 3.1.

With the energy eigenvalues at both instants and the elements of the transition probability matrix we have all the information we need to compute the desired thermodynamic quantities.

4.2 Two q-bit Otto cycle

Now that we have described the working substance of the machine, in this section we study its behavior when submitted to the same Otto cycle described in 3.2. Since some of the calculations are very similar to those of the single q-bit case, we shall present the results more directly.

Point A: We consider again the basis where H_1 is diagonal to compute the average energy. The initial density operator is the thermal state $\rho_A = e^{-\beta_h H_1}/Z_1$. Therefore,

we have

$$E_A = \text{Tr}(\rho_A H_1)$$
$$= -\frac{8Je^{8J\beta_h}}{Z_1} - \frac{2\hbar\omega_1 \sinh(\beta_h\hbar\omega_1)}{Z_1}, \tag{4.24}$$

where

$$Z_1 = 1 + e^{8J\beta_h} + e^{-\beta_h\hbar\omega_1} + e^{\beta_h\hbar\omega_1}. \tag{4.25}$$

Point B: The system is subjected to the work protocol corresponding to a change in the external magnetic field, and the density operator becomes $\rho_B = U\rho_A U^\dagger$, while the Hamiltonian changes from H_1 to H_2. Here, we note that the derivation used in (3.24) to calculate E_B for the single q-bit case remains valid for the coupled case. Again, this energy depends only on the eigenvalues of the Hamiltonian at the initial and final instants and the elements of the transition probability matrix given in (2.9) and (4.23). We have

$$E_B = \text{Tr}(\rho_B H_2)$$
$$= \frac{1}{Z_1} \sum_{i,j} e^{-\beta_h E_j^{(1)}} E_i^{(2)} \left| \left\langle E_i^{(2)} \middle| U \middle| E_j^{(1)} \right\rangle \right|^2$$
$$= -\frac{8Je^{8J\beta_h}}{Z_1} - \frac{2\hbar\omega_2 \sinh(\hbar\omega_1\beta_h)}{Z_1}$$
$$- \frac{\hbar\omega_2}{Z_1}\{-f_1(1-P) + f_2(1-P') - f_3(1-P'')\}, \tag{4.26}$$

where we have defined functions of the system's parameters given by

$$f_1 = 1 + \frac{e^{\beta_h\hbar\omega_1}}{2} - \frac{3e^{-\beta_h\hbar\omega_1}}{2},$$
$$f_2 = \sinh(\beta_h\hbar\omega_1),$$
$$f_3 = \frac{3e^{\beta_h\hbar\omega_1}}{2} - \frac{e^{-\beta_h\hbar\omega_1}}{2} - 1. \tag{4.27}$$

The above are all positive functions for $\beta_h\hbar\omega_1 > 0$ and $\beta_c\hbar\omega_2 > 0$, which are conditions satisfied for this system.

Recall we have expressed E_B in this way because it facilitates the analysis of the adiabatic regime, where $(P, P', P'') \to (1, 1, 1)$. In this limit the term in curly brackets

in 4.27 vanishes and we have

$$E_B^{(ad)} = -\frac{8Je^{8J\beta_h}}{Z_1} - \frac{2\hbar\omega_2 \sinh(\hbar\omega_1\beta_h)}{Z_1}. \tag{4.28}$$

Here the term proportional to J is equal to the one in E_A given in (4.24). Notice, if we make $J = 0$, we recover the result for the single q-bit engine in the adiabatic regime, $E_B^{(ad)} = E_A\omega_2/\omega_1$, as it can easily checked.

Point C: The system thermalizes with the cold source. We have $\rho_C = e^{-\beta_c H_2}/Z_2$ and

$$\begin{aligned}E_C &= \mathrm{Tr}(\rho_C H_2) \\ &= -\frac{8Je^{8J\beta_c}}{Z_2} - \frac{2\hbar\omega_2 \sinh(\beta_c\hbar\omega_2)}{Z_2}.\end{aligned} \tag{4.29}$$

Point D: The magnetic field changes to its initial value and the Hamiltonian changes, in the backward protocol, from H_2 to H_1. As demonstrated in 3.31 and [1], the matrix elements of the transition probability matrix are the same as in the first work protocol. We then have

$$\begin{aligned}E_D &= \mathrm{Tr}(\rho_D H_1) \\ &= \frac{1}{Z_2}\sum_{i,j} e^{-\beta_c E_j^{(2)}} E_i^{(1)} \left|\left\langle E_i^{(1)}\left|\tilde{U}_\tau\right|E_j^{(2)}\right\rangle\right|^2 \\ &= -\frac{8Je^{8J\beta_c}}{Z_2} - \frac{2\hbar\omega_1 \sinh(\hbar\omega_2\beta_c)}{Z_2} \\ &\quad - \frac{\hbar\omega_1}{Z_2}\{-g_1(1-P) + g_2(1-P') - g_3(1-P'')\},\end{aligned} \tag{4.30}$$

with

$$\begin{aligned}g_1 &= 1 + \frac{e^{\beta_c\hbar\omega_2}}{2} - \frac{3e^{-\beta_c\hbar\omega_2}}{2}, \\ g_2 &= \sinh(\beta_c\hbar\omega_2), \\ g_3 &= \frac{3e^{\beta_c\hbar\omega_2}}{2} - \frac{e^{-\beta_c\hbar\omega_2}}{2} - 1.\end{aligned} \tag{4.31}$$

With the average energy at the four points of the cycle, we have all the information necessary to compute the necessary quantities. The heat exchanged with the hot source is given by

$$\begin{aligned}Q_h &= E_A - E_D \\ &= Q_h^{(l)} + Q_h^{(ad)} + Q_h^{(f)},\end{aligned} \tag{4.32}$$

and the three terms are

$$Q_h^{(l)} = 8J\left(\frac{e^{8J\beta_c}}{Z_2} - \frac{e^{8J\beta_h}}{Z_1}\right),$$

$$Q_h^{(ad)} = \hbar\omega_1 \left(\frac{2\sinh\left(\beta_c\hbar\omega_2\right)}{Z_2} - \frac{2\sinh\left(\beta_h\hbar\omega_1\right)}{Z_1}\right)$$

$$= \hbar\omega_1 \left(\frac{e^{\beta_c\hbar\omega_2}}{Z_2} - \frac{e^{-\beta_c\hbar\omega_2}}{Z_2} - \frac{e^{\beta_h\hbar\omega_1}}{Z_1} + \frac{e^{-\beta_h\hbar\omega_1}}{Z_1}\right),$$

$$Q_h^{(f)} = \frac{\hbar\omega_1}{Z_2}\{-g_1(1-P) + g_2(1-P') - g_3(1-P'')\}. \tag{4.33}$$

The part $Q_h^{(l)}$ is proportional to the coupling constant J, but there is also an implicit dependence on the coupling via the partition functions Z_1 and Z_2, which is shared with the other terms as well. This term was also found in the adiabatic description of this machine presented in Ref. [6], where it was interpreted as a heat leak between the two heat reservoirs. It was also shown that this term cannot be harnessed as useful work, but it can improve or decrease the efficiency of the machine, depending on the parameters of the system. We have also $Q_h^{(ad)}$, the part of the heat exchanged that is present even the working substance is driven in a q-adiabatic protocol.

The last term, $Q_h^{(f)}$, is a consequence of a nonadiabatic driving of the working substance. Since the functions g_1, g_2 and g_3 are all positive, this term is an increasing function of the parameters P,P'', and decreasing in P'. This happens because P' is the persistence probability of the instantaneous eigenstate with energy $E_3(t) = 0$. Consequently, we can see that populating states with static energy levels will disrupt the heat exchange, and it can reduce the overall efficiency of the machine.

By considering only the adiabatic terms $Q_h^{(l)}$ and $Q_h^{(ad)}$, we can recover the results presented in [6], where this same thermodynamic cycle was analyzed in the particular case of quantum adiabatic processes in the driving strokes, and a magnetic field with fixed direction. In this reference, they describe the cycle in terms of the occupation probabilities of the thermal states ρ_A and ρ_C at the end of the thermalization strokes. They define them as

$$p_1 = \frac{e^{8J\beta_h}}{Z_1}, \qquad p_2 = \frac{e^{\beta_h\hbar\omega_1}}{Z_1}, \qquad p_3 = \frac{1}{Z_1}, \qquad p_4 = \frac{e^{-\beta_h\hbar\omega_1}}{Z_1},$$

$$p_1' = \frac{e^{8J\beta_c}}{Z_2}, \qquad p_2' = \frac{e^{\beta_c\hbar\omega_2}}{Z_2}, \qquad p_3' = \frac{1}{Z_2}, \qquad p_4' = \frac{e^{-\beta_c\hbar\omega_2}}{Z_2}. \tag{4.34}$$

In the adiabatic limit, the heat exchanged with the hot source is just

$$
\begin{aligned}
Q_h^{(l)} + Q_h^{(ad)} &= 8J\left(\frac{e^{8J\beta_c}}{Z_2} - \frac{e^{8J\beta_h}}{Z_1}\right) \\
&\quad + \hbar\omega_1 \left(\frac{e^{\beta_c\hbar\omega_2}}{Z_2} - \frac{e^{\beta_h\hbar\omega_1}}{Z_1} + \frac{e^{-\beta_h\hbar\omega_1}}{Z_1} - \frac{e^{-\beta_c\hbar\omega_2}}{Z_2}\right) \\
&= 8J(p_1' - p_1) + \hbar\omega_1(p_2' - p_2 + p_4 - p_4'),
\end{aligned}
\tag{4.35}
$$

which is exactly the expression found in [6], where they define $\hbar\omega_1 \equiv 2B$. Since we recover the results of this limiting case, this serves as a consistency check for our description.

To compute the heat exchanged with the cold source, we point out that the expressions of (E_A, E_B) and (E_C, E_D) are symmetrical with respect to the exchange $\hbar\omega_1 \leftrightarrow \hbar\omega_2$ and $\beta_h \leftrightarrow \beta_c$. Because of this, the expressions for the exchanged heats will also have this symmetry. We then have

$$
\begin{aligned}
Q_c &= E_C - E_B \\
&= Q_c^{(l)} + Q_c^{(ad)} + Q_c^{(f)}
\end{aligned}
\tag{4.36}
$$

$$
Q_c^{(l)} = 8J\left(\frac{e^{8J\beta_h}}{Z_1} - \frac{e^{8J\beta_c}}{Z_2}\right),
\tag{4.37}
$$

$$
Q_c^{(ad)} = \hbar\omega_2 \left(\frac{2\sinh(\beta_h\hbar\omega_1)}{Z_1} - \frac{2\sinh(\hbar\omega_2\beta_c)}{Z_2}\right),
\tag{4.38}
$$

$$
Q_c^{(f)} = \frac{\hbar\omega_2}{Z_1}\{-f_1(1 - P) + f_2(1 - P') - f_3(1 - P'')\}.
\tag{4.39}
$$

As in the case of Q_h, the heat exchanged with the cold source is also an increasing function of the persistence probabilities P and P'', and decreasing in P', because f_1, f_2 and f_3 are positive. We can also see that the heat leak term is the negative of the one found for the heat exchange with the hot source, i.e., $Q_c^{(l)} = -Q_h^{(l)}$. Because of this, both terms cancel out in the total work of the cycle, given by

$$
\begin{aligned}
W &= Q_h + Q_c \\
&= Q_h^{(ad)} + Q_c^{(ad)} + Q_h^{(f)} + Q_c^{(f)}.
\end{aligned}
\tag{4.40}
$$

The additional work associated with friction is just the sum of the two heat terms that appear when the driving is not adiabatic, $W^{(f)} = Q_h^{(f)} + Q_c^{(f)}$.

4.3 Operation regions

As discussed in 3.3, the signs of the exchanged energies Q_h, Q_c and W will determine whether the machine will operate as an engine, a thermal accelerator, a refrigerator or as a heater.

One of our aims is to understand how the adiabaticity of the protocol can influence the operation regimes of the machine. For this, we note that the exchanged heats and work (4.32),(4.36) and (4.40) are linear functions of the persistence probabilities P,P' and P'', therefore the zero-level surfaces of these functions are expressions of the type $Q_h = Q_h(P, P', P'') = 0$, and they will represent planes in the domain of (P, P', P'') contained within a cube of unit edges since the coordinates of the points are probabilities (see figures below). For some set of probabilities, given by a point in this space, the heat or work will be positive if the point is above the associated plane and negative if it is below. It is important to notice that not all points in this space represent physical protocols, meaning that there are some values of the persistence probabilities that cannot be associated with any trajectory of the magnetic field. The point $(1, 1, 1)$, that is associated with the adiabatic limit, is always possible for all protocols given that the driving of the magnetic field is slow enough compared to the system's typical time scales. For that reason we highlight this point in the figures ahead.

Since the work is the sum of the heats, the plane associated with $W = 0$ is always between the other two planes. We have then two main distinct cases. In *scenario 1*, the plane associated to $Q_h = 0$ is above the one of $Q_c = 0$, and *scenario 2* is the opposite case. For the first scenario, considering the constraints on the heats and work given by the first and second law of thermodynamics presented in [1], only the heater and refrigerator are possible operation modes. In scenario 2, by the same reasoning, only the engine, accelerator and heater are possible (see 3.3 for the conditions for the operation regimes). In figures 4.1,4.2 and 4.3 we illustrate both scenarios, as well as the intermediate case, where the planes superpose to one another.

4.3.1   The zero coupling limit

The two scenarios mentioned above also appear in the case of a single q-bit, discussed in [1]. There, the situation where $\omega_2/\omega_1 = T_c/T_h$ is associated with the turning point between scenarios 1 and 2. We can recover this result, obtained for a single q-bit machine, if we consider the uncoupled case of our model, corresponding to $J = 0$. In figures 4.1, 4.2 and 4.3 we show the level planes of the exchanged energies for some fixed set of parameters $\hbar\omega_1$ and T_c/T_h as we vary the ratio ω_2/ω_1 from values below, equal, and above T_c/T_h. We define a typical q-bit energy scale E_0 to introduce dimensionless parameters. It can be noted that when the ratios coincide the planes superpose to one another, and only the heater operation mode becomes possible. This is an analogous behavior to the one of the single q-bit. As presented in [1], when $\omega_2/\omega_1 = T_c/T_h$, the operation mode is the heater for any value of the adiabatic parameter. We have verified that, for the uncoupled case of system described here, when the planes superpose, the heater is also the only operation possible for the accessible values of the three adiabatic parameters (P, P', P'').
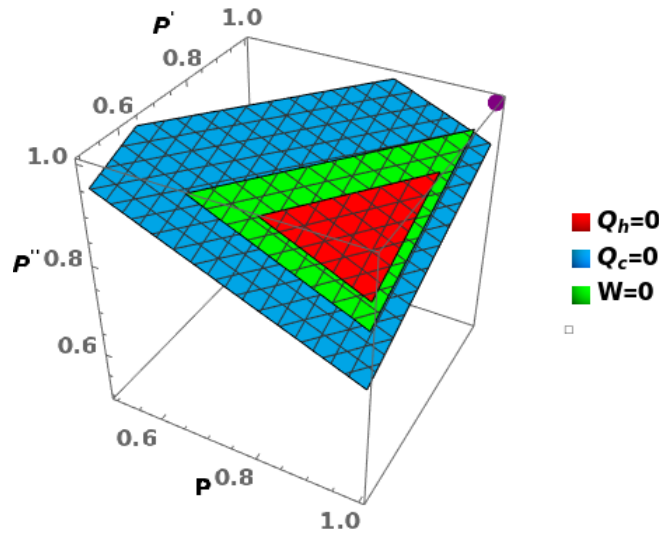

Figure 4.1: Zero level planes of the exchanged heats and work in the zero coupling limit in scenario 1, using the values $\hbar\omega_1/E_0 = 2\sqrt{5}$, $J/E_0 = 0$, $k_b T_h/E_0 = 2$, $T_c/T_h = 0.5$, $\omega_2/\omega_1 = 0.4$. The purple dot indicates the adiabatic limit. In this situation only the heater and refrigerator operations are possible.
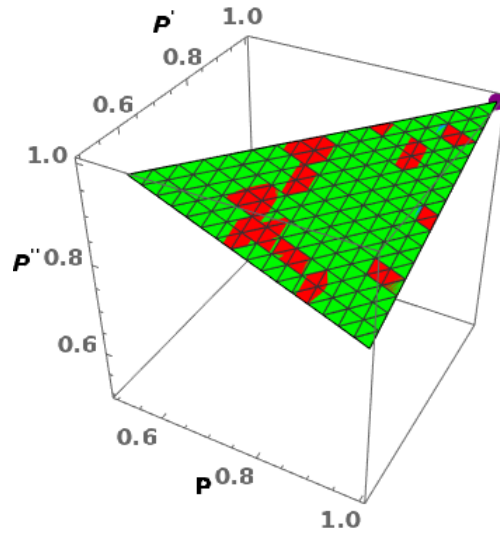
Figure 4.2: Zero level planes of the exchanged heats and work in the zero coupling limit, with the values $\hbar\omega_1/E_0 = 2\sqrt{5}$, $J/E_0 = 0$, $k_b T_h/E_0 = 2$, $T_c/T_h = 0.5$, $\omega_2/\omega_1 = 0.5$. When the ratio between initial and final energies coincides with the ratio between the temperatures of the heat baths, the planes superpose and only the heater becomes possible.
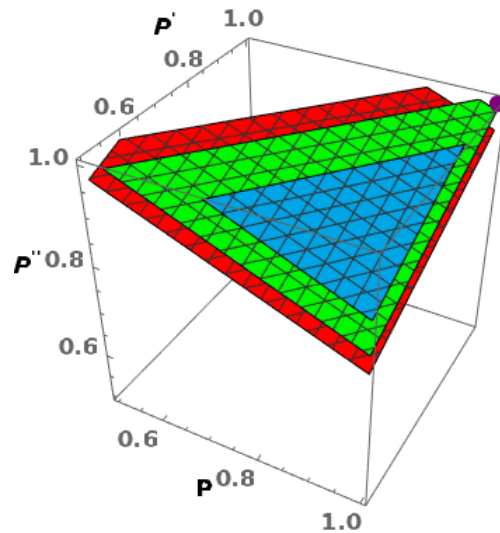

Figure 4.3: Zero level planes of the exchanged heats and work in the zero coupling limit, in scenario 2. Here we use the values $\hbar\omega_1/E_0 = 2\sqrt{5}$, $J/E_0 = 0$, $k_b T_h/E_0 = 2$, $T_c/T_h = 0.5$, $\omega_2/\omega_1 = 0.6$. Here, the heater, accelerator and engine are possible.

4.3.2   The coupled case

The results above are valid only for non-interacting q-bits. If we consider some coupling, the relative position of the planes will vary, as the set of parameters that determine the turning point between scenarios 1 and 2 will also contain J. In figures 4.4, 4.5 and 4.6, we present the same situation of figures 4.1, 4.2 and 4.3 but in the presence of coupling. We can see that the coupling always changes the position of the planes, and by tuning J we can bring the planes close to one another as well as separate them, depending on the other parameters.
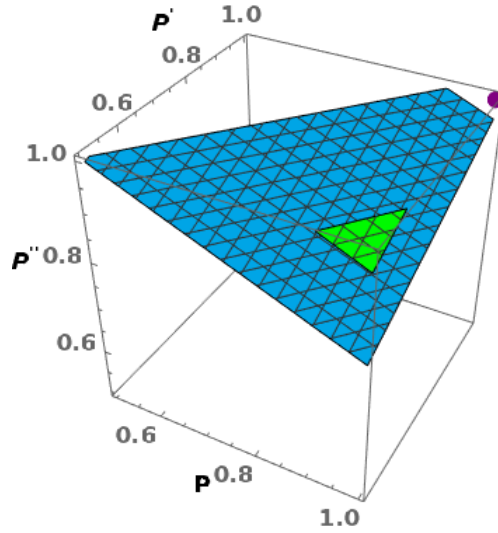

Figure 4.4: Zero level planes of the exchanged heats and work. Here we use the values $\hbar\omega_1/E_0 = 2\sqrt{5}$, $J/E_0 = 1.6$, $k_b T_h/E_0 = 2$, $T_c/T_h = 0.5$, $\omega_2/\omega_1 = 0.4$. The plane associated with $Q_h = 0$ does not appear because it lies outside of the domain where $(P, P', P'') \in [0, 1]$. However, we can assure that we are in scenario 1, because the plane of $W = 0$ is always between the other two. Notice how a moderate modification coupling can alter the position of the planes.
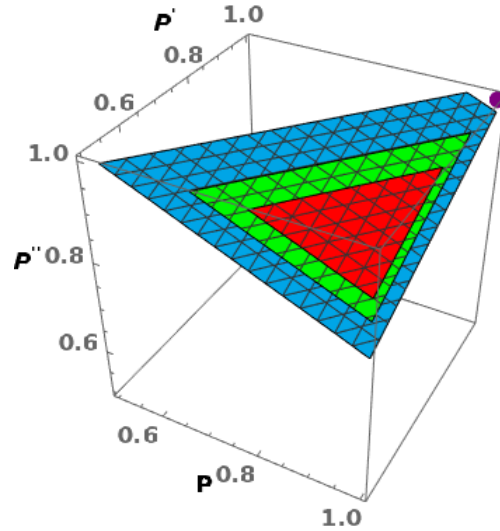
Figure 4.5: Zero level planes of the exchanged heats and work. Here we use the values $\hbar\omega_1/E_0 = 2\sqrt{5}$, $J/E_0 = 1.6$, $k_b T_h/E_0 = 2$, $T_c/T_h = 0.5$, $\omega_2/\omega_1 = 0.5$. Even though $\omega_2/\omega_1 = T_c/T_h$, the planes do not superpose, and this is an exclusive consequence of the coupling
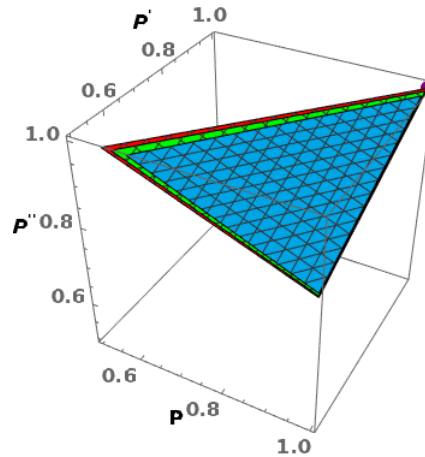

Figure 4.6: Zero level planes of the exchanged heats and work. Here we use the values $\hbar\omega_1/E_0 = 2\sqrt{5}$, $J/E_0 = 1.6$, $k_b T_h/E_0 = 2$, $T_c/T_h = 0.5$, $\omega_2/\omega_1 = 0.6$. We are in scenario 2, with the planes very close to each other. The coupling reduces the possible region for the operation of an engine, even close to the adiabatic limit.

4.4 Hyperbolic tangent protocol with a transverse field

So far we have dealt with the system in a general manner regarding the possible work protocols, or unitary transformations, that can be applied to the working substance. We have left all the information about the specific protocol in the adiabatic parameters (P, P', P''). Now we calculate these quantities explicitly and analyze the results for an specific protocol.

Following the context of two spins driven by an external magnetic field presented in 4.1, we consider a protocol where the field is held constant in the x direction, and varies in the z direction as a hyperbolic tangent function. Therefore, in the expression for the external Hamiltonian presented in 4.2, we have

$$X(t) = \delta, \qquad\qquad Y(t) = 0, \qquad\qquad Z(t) = u(t), \qquad (4.41)$$

where δ and u have dimensions of energy and are proportional to the amplitude of the magnetic field in the x and z directions, respectively. We consider δ to be constant and $u(t)$ is given by

$$u(t) = \frac{1}{2}(u_f - u_i) \tanh\left(\frac{t/t_0 - (t_1 + t_2)/2t_0}{\tau}\right) + \frac{1}{2}(u_f + u_i). \qquad (4.42)$$

In our simulations we make $\delta/E_0 = 1$ and the asymptotic limits are given by $u_i/E_0 = 2$ and $u_f/E_0 = 0$, therefore the initial and final frequencies are $\hbar\omega_1/E_0 = 2\sqrt{5}$ and $\hbar\omega_2/E_0 = 2$ (see (4.3)), which leads to $\omega_2/\omega_1 = 1/\sqrt{5}$. We have have also defined the timescale $t_0 \equiv h/E_0$, where h is Planck's constant. The dimensionless parameter τ is associated with the adiabaticy of the protocol. Indeed, as can be noted from figure 4.7, as τ increases, the variation of the magnetic field takes a larger time interval to occur, and we approach the adiabatic limit as $\tau \to \infty$. We have chosen the hyperbolic tangent function to describe the protocol because it enables us to treat the parameters associated with the initial and final values of the magnetic field u_i and u_f, as well as the adiabatic parameter τ as independent parameters. If we had used a linear function, which is another common choice in this context, the slope of the line, or the rate of the protocol, would depend on the initial and final values of the field.
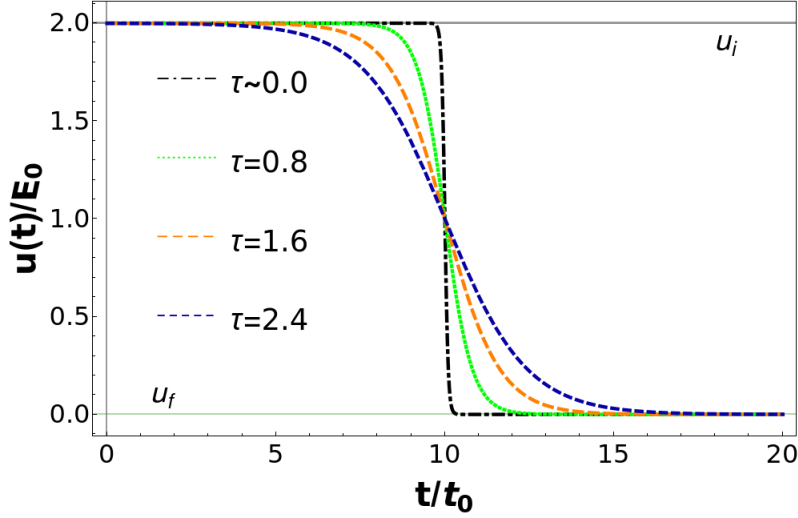
Figure 4.7: Here we show the parameter associated with the magnetic field in the z direction $u(t)/E_0$ as a function of time for $t_1/t_0 = 0$ and $t_2/t_0 = 20$. Note that for larger values of τ the time variation of the field becomes less abrupt.

With the expressions for the time dependent Hamiltonian and the time evolution operator obtained in 4.17 and 4.18, we numerically compute the permanence probabilities defined in 4.1.4 as

$$P = \left| \left\langle E_2^{(2)} \middle| U \middle| E_2^{(1)} \right\rangle \right|^2, \quad P' = \left| \left\langle E_3^{(2)} \middle| U \middle| E_3^{(1)} \right\rangle \right|^2, \quad P'' = \left| \left\langle E_4^{(3)} \middle| U \middle| E_4^{(1)} \right\rangle \right|^2, \quad (4.43)$$

for the given trajectory of the magnetic field.

If we now consider the space of probabilities (P, P', P'') described in the last section, for each possible trajectory determined by the parameters of the external magnetic field (δ, u_i, u_f, τ) and the coupling (J) there will be a point in this space. To study how the adiabaticity of the work protocol can influence the operation regimes of the machine we compute the permanence probabilities for different values of the adiabatic parameter τ and fixed values of the other parameters. Since each value of τ will be associated with a point in the space, a sequence of values of τ will be represented by a parametric trajectory given by the points $(P(\tau), P'(\tau), P''(\tau))$. In the adiabatic limit the three persistence probabilities become unity, or $(P(\tau), P'(\tau), P''(\tau)) \to (1, 1, 1)$ as $\tau \to \infty$. When the curve of this trajectories crosses a zero-level plane of the exchanged energies we have a transition between two operation modes.

In figure 4.8 we show how these transitions occur for some set of the system's

parameters. Since we consider a set of parameters associated with scenario 1, we can see that as the adiabaticity of the protocol increases, the machine changes from a heater to a refrigerator, and therefore we can see that the operation mode of the machine depends directly on the time scale of the work protocol.
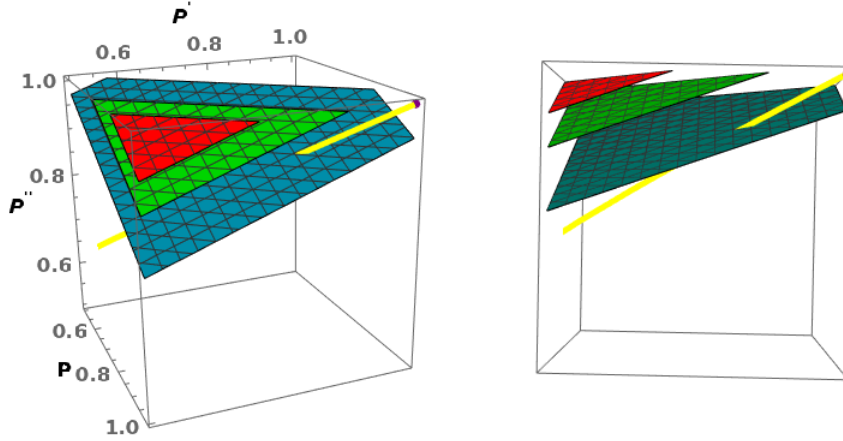

Figure 4.8: The yellow line represents the specific protocol given in Eq. (4.41) associated to variations of the magnetic field (z-direction) with different transition rates given by the parameter τ, while the zero level planes are determined by the following values of the parameters: $J/E_0 = 1, k_b T_h/E_0 = 2, T_c/T_h = 0.5, \omega_2/\omega_1 = 1/\sqrt{5}$. We are in scenario 1. As the adiabatic parameter τ increases, the machine changes the operation region from heater (below the lower plane) to the refrigerator (above the lower plane). We show two angles of the same plot for better visualization of the points where the operation region changes.

It is important to notice that the trajectories in the parameter τ described above depend only on the characteristics of the coupling and the external magnetic field and not on the temperatures of the hot and cold sources T_c and T_h. This happens because the points on the space of probabilities depend only on the instantaneous eigenstates of the Hamiltonian and the time-evolution operator associated with the work protocol, as indicated in the equations in (4.43). As can be seen in the expressions for the exchanged energies in (4.32, 4.36,4.40), these temperatures can modify the position of zero-level planes of the exchanged heats and work, and therefore change the operation mode of the machine once is given a point in the space of persistence probabilities. In figure 4.9 we show the same trajectory of values of τ as the previous case but with different values of T_c and T_h. Accordingly, we can see that we can change between

scenarios 1 and 2 by only changing the temperatures of the heat sources. Another important aspect is that for this set of parameters the operation mode changes from heater, to accelerator and then to engine as the adiabaticity of the protocol increases. It can also be noted that the engine only becomes possible for protocols that are close to the adiabatic limit. In summary, we have seen that both the coupling and the adiabaticity of the protocol, as well as the temperature between the heat sources can influence drastically on the operation mode of the two q-bit thermal machine.
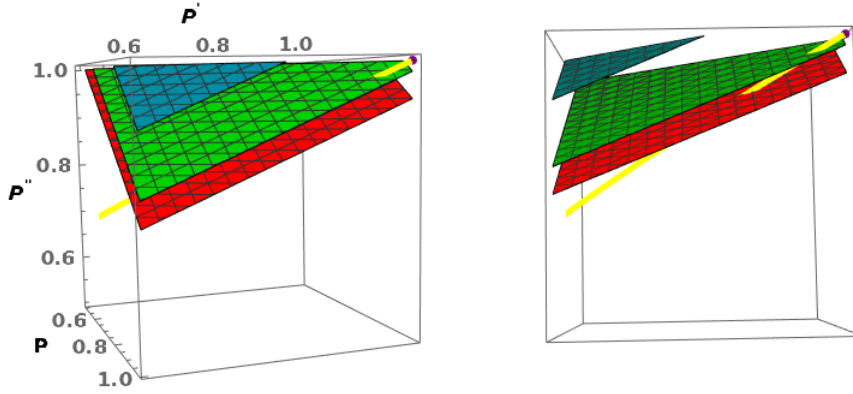

Figure 4.9: The yellow line represents the specific protocol given in Eq. (4.41) associated to variations of the magnetic field (z-direction) with different transition rates given by parameter τ, while the zero level planes are determined by the following values of the parameters: $J/E_0 = 1, k_b T_h/E_0 = 4.7, T_c/T_h = 0.375, \omega_2/\omega_1 = 1/\sqrt{5}$. We have the same trajectory of figure 4.8 but with different bath temperatures T_c and T_h. Here we can have an engine close to the adiabatic limit.

4.4.1 Efficiency of the engine

Now we consider the operation mode of the engine, where $Q_h > 0$, $Q_c < 0$ and $W > 0$. As we have seen in 4.3, this mode can only occur in scenario 2, where the plane associated with $Q_h = 0$ is below the one of $Q_c = 0$.

The efficiency of an engine, also known as coefficient of performance, is the ratio between the useful work delivered by the machine to the heat withdrawn from the hot source, $W/Q_h = 1 + Q_c/Q_h$. We can compute the efficiency directly from the expressions of Q_h and Q_c given in (4.32,4.36), with the permanence probabilities calculated for the protocol described above. In figure 4.10 we show the efficiency normalized by the Carnot efficiency $\eta_c = 1 - T_c/T_h$ as a function of τ, and we consider only values of τ for which the machine operates as an engine. We can see that the efficiency grows as the system approaches the adiabatic limit, which agrees with the idea of the trade-off between power and efficiency, also present in classical heat engine analysis. We can also see that the efficiency has an upper bound that is lower than the Carnot efficiency. For the particular case where the magnetic field is fixed in one direction and the work protocol is adiabatic this upper bound has been found analytically [6].
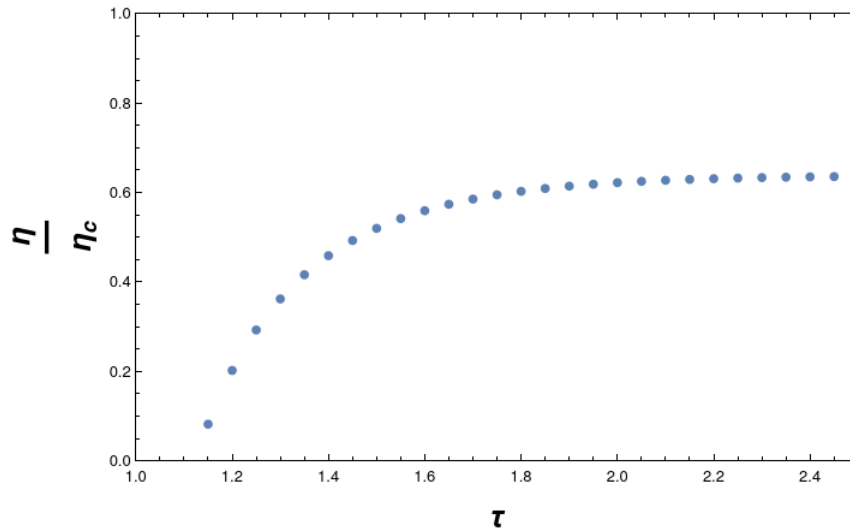

Figure 4.10: Efficiency normalized by the Carnot efficiency, $1-T_c/T_h$, as a function of τ following the values of the parameters $J/E_0 = 1, k_b T_h = 4.7, T_c/T_h = 0.375, \omega_2/\omega_1 = 1/\sqrt{5}$.

In this chapter we have seen how the coupling and the possibility of nonadiabatic driving of the working substance can alter greatly the operation regions of the two q-bit thermal machine. We have also seen how the efficiency of an engine operating in this cycle depends on the rate in which the work protocol is performed. In the future, we wish to investigate what domain of these parameters maximizes the efficiency, and in which mode of operation the advantage is greater.

Chapter 5

Conclusions

In this work we presented basic concepts of quantum thermodynamics, like heat and work, and also a formalism to compute these quantities for thermal machines composed of spin systems with one and two components.

For two interacting spins, we have presented original results, showing how the coupling and the nonadiabatic driving of the working substance can affect the efficiency and operation modes of the machine. We have expanded the analysis of [1] by considering a coupled working substance, and we also generalized the analysis in [6] because we considered an external magnetic field that can vary in direction as well as intensity. Depending on the temperatures of the heat sources, the coupling parameter, as well as the initial and final values of the magnetic field, we have seen that the machine can change from a heater to an accelerator to an engine, or from a heater to a refrigerator as the adiabaticity of the work protocol increases.

In the remainder of this conclusion chapter, we mention other possible analysis that can be made on quantum thermal machines that are present in the literature, and could provide greater insight over the model analyzed here, as well as others.

5.1   The definition of quantum work and heat

Starting from a more fundamental consideration, it is important to notice that the definitions of work and heat used so far (chapter 2) can be restrictive when it comes to important properties like quantum coherence in the energy basis. If we define work and heat only within the two-point measurement scenario, the information about this

important property will be lost during the projective measurements. Therefore, in this formalism, we cannot investigate the advantages that an initially coherent working substance could provide. This is a considerable limitation on the description, since coherence is a central resource in quantum theory, and one the most sought properties of quantum technological devices.

There is a recent work [32] that brings an interesting solution to this problem. The authors have used Bayesian networks, a concept known in statistics and computer science, to define quantum fluctuations relations for the heat exchange that take initial coherence in the energy basis of the working substance into account. Moreover, these results have been experimentally verified [33]. This more general definition of heat is more suitable for small interacting systems such as the ones described in the previous chapters, and this investigation is a good lead for future projects.

Even within the two-point measurement scenario, we still made our analysis particular, since we only considered the averages of the heat and work exchanged, which depend only on the expectation value of the Hamiltonian at the four points of the cycle. Since we are describing small quantum systems, the quantum fluctuations in the computed quantities can be quite large compared to their average values, therefore a description only in terms of average values can be inaccurate. It is common in the literature to perform energy calculations in the same way as in here, but it is a restriction worth mentioning. To obtain the complete information on these fluctuations, it would be important to consider the probability distributions for work and heat, presented in (2.12) and (2.24), respectively, as well as the fluctuations theorems, like Jarzynski's equality. It is another interesting possibility to investigate the effects of coupling and nonadiabatic drivings over these probability distributions for the coupled spin system described here.

5.2 Entropy Considerations

Anyone familiar with the fields of quantum and classical thermodynamics might have missed some important quantity in this text, and that is entropy. In the analysis of classical thermal machines, computing the change in entropy between the points of the given cycle is usually an important step of the description of more complicated

machine cycles. Moreover, entropy is also useful for describing dissipative processes, since irreversible protocols produce additional entropy by driving the system beyond the relaxation rate, and this entropy is usually associated with dissipation of heat.

For general quantum analysis, and specially in thermodynamics, the entropies of density operators, like the Von Neumann entropy, are also present. Their definition comes from the quantum information point of view, in an analogous way as the Shannon entropy is defined for probability distributions in classical information theory.

In principle, these "information" entropies do not presume any physical thermodynamic system to be defined [27]. Nonetheless, by the means of statistical and quantum mechanics we are able to describe macro and microscopic systems by probability distributions and density operators, and consequently, there will be entropies associated with the information content of these systems. In some particular cases that are quite common, the thermodymamic entropy coincides with some entropy of the associated probability distribution or density operator. Indeed, there is a deep connection between information and thermodynamics, which is elegantly demonstrated by the Landauer Principle [34], which states that erasing information causes a fundamental and very small increase in the overall entropy of the systems involved.

The so called information thermodynamics perspective was also used in the study of quantum heat engines [35], and other information theory concepts are also useful in this context. In [36], they associate the irreversible work of the system directly to the aforementioned "*quantum friction*", that can be caused by the non-commutativity of the Hamiltonian at different times, and is associated with the production of entropy in the energy basis. They have also shown that the irreversible work can be expressed as the relative entropy between the density operator at the end of the work protocol and the density operator at the end of the associated adiabatic process. Since we have found terms in the exchanged heats associated with inner friction, (see 4.2).

5.3   The limitations of the model

The isotropic interaction chosen in 4.1.2 and also used in ([6],[9]), can be considered a restrictive model. The reason for this is that the operator representing the interaction term is proportional to the identity, and even null in the subspace where the dynamics

is non-trivial (the triplet subspace, 4.1.2). By this, we can expect that, for this system, the coupling effects will be minor compared to the ones of more complicated interaction models. One of our goals is to generalize the formalism used here for these other systems.

Another particularity of our description is the choice of the Otto cycle, that can be unrealistic, by considering only complete thermalizations strokes and pure unitary transformations in the work protocols. If we wait for the system to thermalize completely with the heat reservoirs, the cycle of the machine will take, in principle, infinite time. To perform cycles in finite time, it is necessary to perform partial thermalizations, and this requires an analysis of the detailed structure of the heat baths, by the means of the theory of open quantum systems. An analysis of a different model that describes these ideas is presented in [31]. Notice, in this work we only focused on the consequences of performing the work protocols at finite-time (nonadiabatic), but considering more realistic thermal interactions is equally important.

Still regarding the work strokes. We have considered the case where the working substance is completely isolated from the heat baths in these strokes, and therefore the evolution is only due to the time varying Hamiltonian (unitary). For experimental considerations, we must always consider some kind of heat transfer, since no system can be truly isolated from its surroundings. One option to avoid this issue is performing work strokes during a time interval much smaller then the relaxation time of the system. In this case, there will be no time available for the substance to thermalize with the baths. In this particular scenario, we can safely consider the dynamics as purely unitary. Because nuclear spins usually interact weakly with thermal baths, they are a good option for experimental implementations of these protocols. In [37], a NMR setup is used to reconstruct the work distribution for operations on a single q-bit system. The authors have also implemented an Otto cycle in this framework [38].

5.4   Final remarks

Even with all the approximations considered, we have found interesting results concerning the effects of coupling and non-adiabaticity in the operation of quantum ther-

mal machines. It is important to notice that the formalism presented here can be used to a variety of systems like, for example, more complex interaction models for spin systems, or systems of harmonic oscillators. It is possible to generalize the idea of the planes associated with the zero value of the heats and work, as well as trajectories of different values of adiabaticity, to systems with more energy levels. The geometrical considerations regarding the 3-dimensional probability space in 4.3 can still be made for spaces of more dimensions, with only more complex objects, such as hyperplanes.

The field of quantum thermodynamics is highly linked with the development of better, or more efficient, quantum devices, and therefore experimental implementations are much needed. In future works, we seek to verify, in the laboratory, the results presented here and, contribute more to the revolution brought by the new quantum technologies.

Appendix A

Composition of two elements of a Lie Algebra

In this discussion we will use the the factorization method already presented in eq. (1.19) as well as the usual Baker-Campbell-Hausdorff (BCH) relations, namely

$$e^A B e^{-A} = B + [A, B] + \frac{1}{2!}[A, [A, B]] + ..., \tag{A.1}$$

$$e^A f\left(\hat{C}\right) e^{-A} = f\left(e^A \hat{C} e^{-A}\right), \tag{A.2}$$

to find the composition of two G operators used in 1.3. This derivation is also based in [13].

We start by inserting the identity operator, conveniently represented as $\mathbb{1} = e^{\Lambda_{1+}} e^{-\Lambda_{1+}}$, to the right of the operator $e^{\ln \Lambda_{2c}}$ in equation (1.23). We then get

$$G(\mathbf{\Lambda}_2)G(\mathbf{\Lambda}_1) = e^{\Lambda_{2+}T_+} e^{\ln(\Lambda_{2c})T_c} e^{\Lambda_{1+}T_+} \cdot$$

$$\cdot \left\{ e^{-\Lambda_{1+}T_+} e^{\Lambda_{2-}T_-} e^{\Lambda_{1+}T_+} \right\} \cdot e^{\ln(\Lambda_{1c})T_c} e^{\Lambda_{1-}T_-}. \tag{A.3}$$

We can simplify the term in curly brackets using the BCH relations. We start by associating $f(x) \to e^{\Lambda_{2-}x}$, $A \to -\Lambda_{1+}T_+$ and $\hat{C} \to e^{\Lambda_{2-}T_-}$ in eq. (A.2) as follows:

$$e^{-\Lambda_{1+}T_+} e^{\Lambda_{2-}T_-} e^{\Lambda_{1+}T_+} = f\left(e^{-\Lambda_{1+}T_+} \cdot (\Lambda_{2-}\hat{T_-}) \cdot e^{\Lambda_{1+}T_+}\right) \tag{A.4}$$

$$= \exp\{\Lambda_{2-}(e^{-\Lambda_{1+}T_+} T_- e^{\Lambda_{1+}T_+})\}.$$

Now we can apply eq. (A.1) on the term in braces by making $B \to T_-$. For that we need the commutators

$$[A, B] = -\Lambda_{1+}[T_+, T_-] \tag{A.5}$$

$$= 2\epsilon\Lambda_+ T_c,$$

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$$[A, [A, B]] = -2\epsilon(\Lambda_{1+})^2 [T_+, T_c] \tag{A.6}$$

$$= 2\epsilon\delta(\Lambda_{1+})^2 T_+,$$

$$[A, [A, [A, B]]] = -2\epsilon\delta(\Lambda_{1+})^3 [T_+, T_+] = 0. \tag{A.7}$$

In the BCH formula (A.1), which is an infinite series, the next therm is always proportional to the commutator of A with the previous term. Therefore, because the fourth term vanishes, all the subsequent terms will vanish as well. We are left with the result

$$e^{-\Lambda_{1+}T_+} e^{\Lambda_{2-}T_-} e^{\Lambda_{1+}T_+} = \exp\left\{\Lambda_{2-}\left(T_- + 2\epsilon\Lambda_{1+}T_c + \epsilon\delta(\Lambda_{1+})^2 T_+\right)\right\} \tag{A.8}$$

$$= e^{\sigma_+ T_+ + \sigma_c T_c + \sigma_- T_-}$$

$$= e^{\Sigma_+ T_+} e^{\ln(\Sigma_c) T_c} e^{\Sigma_- T_-}$$

with

$$\sigma_+ = \epsilon\delta(\Lambda_{1+})^2 \Lambda_{2-} \quad, \quad \sigma_c = 2\epsilon\Lambda_{2-}\Lambda_{1+} \quad \text{and} \quad \sigma_- = \Lambda_{2-}. \tag{A.9}$$

In the last step we have used the factorization procedure given in (1.19). The coefficients are given by

$$\Sigma_c = \left(\cosh(\nu') - \frac{\delta\sigma_c}{2\nu'}\sinh(\nu')\right)^{-\frac{2}{\delta}} \quad \text{and} \quad \Sigma_\pm = \frac{2\sigma_\pm \sinh(\nu')}{2\nu'\cosh(\nu') - \delta\sigma_c \sinh(\nu')}, \tag{A.10}$$

with ν' given by

$$\nu'^2 = (\frac{\delta\sigma_c}{2})^2 - \delta\epsilon\sigma_+\sigma_-. \tag{A.11}$$

By replacing (A.9) in A.11 we can easily see that $\nu' = 0$. However, if we insert this result directly in the expressions for the Σ coefficients we arrive at indeterminate terms. Instead we take the limit, already substituting the values of σ_+, σ_c and σ_-

$$\Sigma_c = \left(1 - \epsilon\delta\Lambda_{2-}\Lambda_{1+}\left\{\lim_{\nu\to0}\frac{\sinh(\nu)}{\nu}\right\}\right)^{-\frac{2}{\delta}} = (1 - \epsilon\delta\Lambda_{2-}\Lambda_{1+})^{-\frac{2}{\delta}}, \tag{A.12}$$

$$\Sigma_+ = \frac{2\epsilon\delta(\Lambda_{1+})^2\Lambda_{2-}\left\{\lim_{\nu\to0}\frac{\sinh(\nu)}{\nu}\right\}}{2 - 2\epsilon\delta\Lambda_{2-}\Lambda_{1+}\left\{\lim_{\nu\to0}\frac{\sinh(\nu)}{\nu}\right\}} = \frac{\epsilon\delta(\Lambda_{1+})^2\Lambda_{2-}}{1 - \epsilon\delta\Lambda_{2-}\Lambda_{1+}}, \tag{A.13}$$

$$\Sigma_- = \frac{2\Lambda_{2-}\left\{\lim_{\nu\to 0}\frac{\sinh(\nu)}{\nu}\right\}}{2 - 2\epsilon\delta\Lambda_{2-}\Lambda_{1+}\left\{\lim_{\nu\to 0}\frac{\sinh(\nu)}{\nu}\right\}} = \frac{\Lambda_{2-}}{1 - \epsilon\delta\Lambda_{2-}\Lambda_{1+}}. \tag{A.14}$$

Now that we know the values of these coefficients, we can proceed by inserting (A.8) in (A.3) to get

$$\begin{aligned}
G(\mathbf{\Lambda}_2)G(\mathbf{\Lambda}_1) &= e^{\Lambda_{2+}T_+}e^{\ln(\Lambda_{2c})T_c}e^{\Lambda_{1+}T_+}\cdot \\
&\quad \cdot \left\{e^{\Sigma_+T_+}e^{\ln(\Sigma_c)T_c}e^{\Sigma_-T_-}\right\}\cdot e^{\ln(\Lambda_{1c})T_c}e^{\Lambda_{1-}T_-} \\
&= e^{\Lambda_{2+}T_+}e^{\ln(\Lambda_{2c})T_c}e^{(\Lambda_{1+}+\Sigma_+)T_+}e^{\ln(\Sigma_c)T_c}e^{\Sigma_-T_-}e^{\ln(\Lambda_{1c})T_c}e^{\Lambda_{1-}T_-}.
\end{aligned} \tag{A.15}$$

Observe how we successfully grouped two operators with T_+ in the exponent.

Now we wish to move the operators with T_c in the exponent to the center of the expression. As before, this can be done by inserting the identity, now represented as $\mathbb{1} = e^{-\ln\Lambda_{2c}}e^{\ln\Lambda_{2c}}$, to the left of the operator $e^{\ln\Sigma_c T_c}$ in A.15. This leads to

$$\begin{aligned}
G(\mathbf{\Lambda}_2)G(\mathbf{\Lambda}_1) &= e^{\Lambda_{2+}T_+}\cdot\left\{e^{\ln(\Lambda_{2c})T_c}e^{(\Lambda_{1+}+\Sigma_+)T_+}e^{-\ln(\Lambda_{2c})T_c}\right\}\cdot e^{\ln(\Lambda_{2c}\Sigma_c)T_c}\cdot \\
&\quad \cdot e^{\Sigma_-T_-}e^{\ln(\Lambda_{1c})T_c}e^{\Lambda_{1-}T_-},
\end{aligned} \tag{A.16}$$

Here we have used that $e^{\ln\Lambda_{2c}T_c}e^{\ln\Sigma_c T_c} = e^{\ln(\Lambda_{2c}\Sigma_c)T_c}$, which is valid since the operator T_c obviously commutes with itself and the properties of the sum of logarithms still hold for logarithms of operators.

Just as before, we proceed by applying the BCH relations to the term in curly braces. First, we use (A.2) to get

$$e^{\ln(\Lambda_{2c})T_c}e^{(\Lambda_{1+}+\Sigma_+)T_+}e^{-\ln(\Lambda_{2c})T_c} = \exp\{(\Lambda_{1+}+\Sigma_+)\cdot(e^{\ln(\Lambda_{2c})T_c}T_+e^{-\ln(\Lambda_{2c})T_c})\}. \tag{A.17}$$

To apply the BCH formula (A.1) on the left-hand side of the equation above with $A \to \ln(\Lambda_{2c})T_c$ and $B \to T_+$ we need the commutators

$$\begin{aligned}
[A, B] &= \ln(\Lambda_{2c})[T_c, T_+] \\
&= \delta\ln(\Lambda_{2c})T_+,
\end{aligned} \tag{A.18}$$

$$\begin{aligned}
[A, [A, B]] &= \delta(\ln(\Lambda_{2c})^2[T_c, T_+] \\
&= \delta^2(\ln(\Lambda_{2c}))^2 T_+,
\end{aligned} \tag{A.19}$$

$$[A, [A, [A, B]]] = \delta^3(\ln(\Lambda_{2c}))^3 T_+. \tag{A.20}$$

In this case the series does not truncate, and we have to account for all the infinite terms to proceed. However, we can see a clear pattern, as every new commutator is equal to the last one multiplied by a factor $\delta \ln(\Lambda_{2c})$. We therefore can write

$$e^{\ln(\Lambda_{2c})T_c} T_+ e^{-\ln(\Lambda_{2c})T_c} = T_+ + \delta \ln(\Lambda_{2c})T_+ + \frac{1}{2!}(\delta \ln(\Lambda_{2c}))^2 T_+ + ... \tag{A.21}$$

$$= \left[\sum_{n=0}^{\infty} \frac{(\delta \ln \Lambda_{2c})^n}{n!} \right] T_+, \tag{A.22}$$

$$= (\Lambda_{2c})^\delta T_+. \tag{A.23}$$

By inserting this result in (A.17) and then in (A.16), we find that

$$G(\mathbf{\Lambda}_2)G(\mathbf{\Lambda}_1) = e^{\Lambda_{2+}T_+} \cdot \left\{ e^{(\Lambda_{1+}+\Sigma_+)\Lambda_{2c}^\delta T_+} \right\} \cdot e^{\ln(\Lambda_{2c}\Sigma_c)T_c} \cdot$$

$$\cdot e^{\Sigma_- T_-} e^{\ln(\Lambda_{1c})T_c} e^{\Lambda_{1-}T_-} \tag{A.24}$$

$$= e^{[\Lambda_{2+}+(\Lambda_{1+}+\Sigma_+)\Lambda_{2c}^\delta]T_+} e^{\ln(\Lambda_{2c}\Sigma_c)T_c} e^{\Sigma_- T_-} e^{\ln(\Lambda_{1c})T_c} e^{\Lambda_{1-}T_-}.$$

Now we must move the operators with T_c in the exponent to the center of the expression. This can be done by inserting the identity, now represented as $\mathbb{1} = e^{\ln(\Lambda_{1c})T_c} e^{-\ln(\Lambda_{1c})T_c}$ to the left of the operator $e^{\Sigma_- T_-}$ in the expression above, leading to

$$G(\mathbf{\Lambda}_2)G(\mathbf{\Lambda}_1) = e^{[\Lambda_{2+}+(\Lambda_{1+}+\Sigma_+)\Lambda_{2c}^\delta]T_+} e^{\ln(\Lambda_{2c}\Sigma_c)T_c} \cdot$$

$$\cdot e^{\ln(\Lambda_{1c})T_c} \cdot \left\{ e^{-\ln(\Lambda_{1c})T_c} e^{\Sigma_- T_-} e^{\ln(\Lambda_{1c})T_c} \right\} \cdot e^{\Lambda_{1-}T_-}, \tag{A.25}$$

To treat the term in curly braces we proceed analogously as in (A.17) to (A.23). Since the derivation is almost identical, we proceed by presenting the result

$$G(\mathbf{\Lambda}_2)G(\mathbf{\Lambda}_1) = e^{[\Lambda_{2+}+(\Lambda_{1+}+\Sigma_+)\Lambda_{2c}^\delta]T_+} e^{\ln(\Lambda_{1c}\Lambda_{2c}\Sigma_c)T_c} \cdot$$

$$\cdot e^{(\Sigma_-\Lambda_{1c}^\delta+\Lambda_{1-})T_-}. \tag{A.26}$$

Now replacing the Σ's using (A.12), (A.13) and (A.14) we arrive to the final result

$$G(\mathbf{\Lambda}_2)G(\mathbf{\Lambda}_1) = e^{\alpha_2 T_+} e^{\ln(\beta_2)T_c} e^{\gamma_2 T_-}, \tag{A.27}$$

with

$$\alpha_2 = \Lambda_{2+} + \frac{\Lambda_{1+}(\Lambda_{2c})^{\delta}}{1 - \epsilon\delta\Lambda_{1+}\Lambda_{2-}},$$

$$\beta_2 = \frac{\Lambda_{1c}\Lambda_{2c}}{(1 - \epsilon\delta\Lambda_{1+}\Lambda_{2-})^{\frac{2}{\delta}}}, \qquad (A.28)$$

$$\gamma_2 = \Lambda_{1-} + \frac{\Lambda_{2-}(\Lambda_{1c})^{\delta}}{1 - \epsilon\delta\Lambda_{1+}\Lambda_{2-}}.$$

We have finally reduced the composition of two arbitrary elements of the given Lie algebras to a single element. This results are called the New BCH-like relations.

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