Thermodynamics and Quantum Correlations

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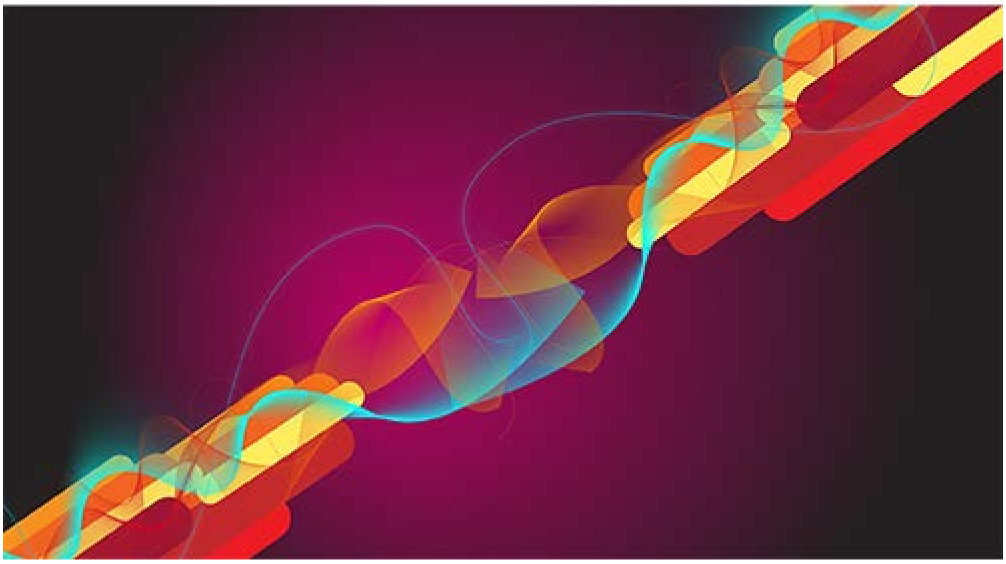

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Abstract

Thermodynamics traditionally deals with macroscopic systems at thermal equilibrium. However, since the very beginning of the theory, its range of applicability has only increased, nowadays being applied to virtually every field of science, and to systems of extremely different size.

This thesis is devoted to the study of thermodynamics in the quantum regime. It contains original results on topics that include: Work extraction from quantum systems, fluctuations of work, the energetic value of correlations and entanglement, and the thermodynamics of closed quantum many body systems.

First, we study work extraction from thermally isolated systems. Here the notion of passive states naturally arises, as those quantum states from which no work can be extracted. We start by characterising the set of passive states, and find the most energetic passive states, a dual family to the well known Gibbs (or thermal) states. Remarkably, passive states have the property of activation: When considered as a whole, several copies of passive states can become nonpassive. We study the dynamics of activation processes, and find a relation between the entanglement generated and the speed of the process.

Next, we consider the possibility of extracting work from a system using an auxiliary thermal bath. In this case, according to the second law of thermodynamics, the amount of work is bounded by the free energy difference. We develop corrections to this law which arise from the finite size and the structure of the bath.

We go on by studying the fluctuations of work. Fluctuations are particularly relevant for small systems, where their relative size is comparable to the average value itself. However, characterising the fluctuations in the quantum regime is particularly difficult, as measurements generically disturb the state. In fact, we derive a no go result, showing that it is not possible to exactly measure the fluctuations of work in quantum coherent processes. Despite this result, we develop a new scheme that allows for their approximate measurement.

An important part of this thesis is devoted to the relation between quantum correlations and work. We start by considering a set of correlated states which are thermal at the local level, in which case the extractable work can only come from the correlations. We compute the amount of work that can be

stored in entangled, separable and correlated states with a fixed entropy, by finding the corresponding optimal states and protocols. These results provide fundamental bounds on the potential of different type of correlations for work storage and extraction. Next, we consider the converse scenario, and study the creation of correlations from thermal states. We find thresholds on the maximal temperature for the generation of entanglement. We also work out the minimal work cost of creating different types of correlations, including total correlations, entanglement, and genuine multipartite entanglement.

Finally, we study the thermodynamics of closed quantum systems. Here we use one of the most important recent insights from the study of equilibration in quantum systems: Closed many body systems do not equilibrate, but can be effectively described as if they had equilibrated when looking at a restricted, physically relevant, class of observables. Importantly, the corresponding equilibrium state is not necessarily a Gibbs state, but may be very well given by a Generalized Gibbs ensemble state. With this in mind, we develop a framework for studying entropy production and work extraction in closed quantum systems.

List of publications

Publications forming part of the thesis

- *Entanglement Generation is Not Necessary for Optimal Work Extraction*, Karen V. Hovhannisyan, Martí Perarnau-Llobet, Marcus Huber, and Antonio Acín, Physical Review Letters **111**, 240401 (2013).

- *Thermodynamic cost of creating correlations*, Marcus Huber, Martí Perarnau-Llobet, Karen V. Hovhannisyan, Paul Skrzypczyk, Claude Klöck, Nicolas Brunner, and Antonio Acín, New Journal of Physics **17**, 065008 (2015).

- *Extractable work from correlations*, Martí Perarnau-Llobet, Karen V. Hovhannisyan, Marcus Huber, Paul Skrzypczyk, Nicolas Brunner, and Antonio Acín, Physical Review X **5**, 041011 (2015).

- *The thermodynamics of creating correlations: Limitations and optimal protocols*, David Edward Bruschi, Martí Perarnau-Llobet, Nicolai Friis, Karen V. Hovhannisyan, and Marcus Huber, Physical Review E **91**, 032118 (2015).

- *Most energetic passive states*, Martí Perarnau-Llobet, Karen V. Hovhannisyan, Marcus Huber, Paul Skrzypczyk, Jordi Tura, and Antonio Acín, Physical Review E **92**, 042147 (2015).

Preprints forming part of the thesis

- *Work and Entropy Production in Generalised Gibbs Ensembles*, Martí Perarnau-Llobet, Arnau Riera, Rodrigo Gallego, Henrik Wilming, Jens Eisert, arXiv:1512.03823 (2015). Submitted to PRX.

- *Energetics of correlations in interacting systems*, Nicolai Friis, Marcus Huber, Martí Perarnau-Llobet, arXiv:1512.03823 (2015). Accepted in PRE.

Publications relevant to the Thesis, but not forming part of it

- *The entropy vector formalism and the structure of multidimensional entanglement in multipartite systems*, Marcus Huber, Martí Perarnau-Llobet, and Julio I. de Vicente, Physical Review A **88**, 042328 (2013).
- *Locality of temperature in spin chains*, Senaida Hernández-Santana, Arnau Riera, Karen V Hovhannisyan, Martí Perarnau-Llobet, Luca Tagliacozzo and Antonio Acín, New Journal of Physics **17**, 085007 (2015).

Contents

1. Introduction

Quantum physics emerged at the beginning of the 20th century in order to describe new microscopic phenomena involving, for example, atoms and photons. The theoretical models at that time, based on Newton's laws and Maxwell equations, were unable to provide descriptions to several phenomena, such as the black body radiation or the photoelectric effect. Quantum mechanics emerged as a new microscopic theory that could describe such new phenomena. The result was a genuinely new physical theory, which started a new paradigm in science. The theory was equally successful and debated. It yield exact predictions to the experimental results. However, its very foundations, and in particular the interpretation of the theory, was not settled from the early days of the theory and remains unsettled today.[1]

Quantum physics is intrinsically probabilistic: It does not provide a deterministic answer to an experiment, but only assigns a probability to the different possible outcomes. The measurement apparatus has an active role, so that the possibility of observing basic physical properties, such as the position or the velocity, without disturbing them vanishes. Not only that, but fundamental ingredients of the theory, such as the superposition principle or entanglement, completely escape our intuition. These unique features have both fascinated and troubled quantum physicists for many decades, and a common attitude towards the foundations of quantum physics was summarised by the celebrated quote, *shut up and calculate.*

A new mindset in quantum physics started in the 80's and 90's with the raise of quantum information and quantum computation. The crucial realisation was that quantum physics had the potential to revolutionise information technologies. Quantum effects, which challenged our conceptions of nature and reality, became powerful resources to improve current technologies. Celebrated examples include Shor's algorithm to factor large numbers efficiently, and the BB84 protocol for secure communication using quantum entanglement. These theoretical proposals were combined with an extreme advance in the control

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[1] There are different interpretations of quantum theory, including The Copenhagen interpretation, many-worlds interpretation, pilots-wave interpretation (Bohmian mechanics) and information-based interpretations. Up until now,The Copenhagen interpretation is the most used one.

and manipulation of quantum systems in experimental platforms, such as ion traps and cold atoms.

This success has motivated a renewed interest in the implications of and possibilities offered by quantum phenomena in different fields. In particular, recent years have experienced a growing interest in the study of thermodynamics in the quantum regime (see (GHR$^+$16; VA15) for recent reviews in quantum thermodynamics). Thermodynamics, the study of energy transfers in form of work and heat, started in the XVIIth century with a very practical motivation: The design and development of heat engines. Approximately two centuries later, in the 1950s, the first and second laws of thermodynamics were developed, primarily out of the works of William Rankine, Rudolf Clausius, and William Thomson. These laws, which were originally formulated for heat engines, rapidly increased its range of applicability. In fact, nowadays, the laws of thermodynamics, closely together with methods from statistical physics, are applied to virtually every field of science, from black holes and cosmology, to biology and chemistry.

Due to the universality of the laws of thermodynamics, we should not be surprised that quantum physics obeys them within its framework of applicability. The question is in fact how wide is this range. Standard thermodynamics is formulated for states in thermal equilibrium, but current research suggests that its power of predictability goes way beyond them. For example, recent results coming from quantum information theory show that pure quantum states of sufficiently large systems behave, for most times and observables, effectively as thermal equilibrium states (see (GE15) for a review on the topic of equilibration). Furthermore, different approaches to deal with out of equilibrium thermodynamic processes, in particular those based on resource theories (BaHO$^+$13) and fluctuation theorems (TLH07), confirm the validity of the second law for a wide range of transformations. These works open exciting possibilities and provide powerful tools to explore and study the thermodynamics of small quantum systems.

The fact that quantum physics satisfies the laws of thermodynamics by no means implies that quantum effects cannot modify, or even enhance, certain thermodynamic tasks. In fact, the main goal of this thesis is to understand and explore the implications of quantum phenomena, such as coherence and entanglement, in thermodynamics.

1.1. Motivation and contributions

1.1.1. Work extraction from quantum systems

State of the art and motivation

A considerable part of the thesis is devoted to the study of work extraction in the quantum regime. Work extraction, together with other tasks in thermodynamics, is traditionally studied within the set of thermodynamic operations, which consists of transformations of thermodynamic variables, such as volume, temperature, etc. Those operations can be implemented with ignorance of any microscopic information, and indeed they are easily implementable in real applications. In fact, all engines are based on them. When dealing with small quantum systems, it is not always clear what a thermodynamic operation is. A way to escape this problem is to consider instead *all* operations as thermodynamic operations. The motivation for this approach is two fold:

- The number of degrees of freedom of the systems of interest in the quantum regime can be small. In this case, it is conceivable to treat all degrees of freedom in the same footing, and assume we can transform all of them.
- In the last decades we have experienced an enormous advance in the level of experimental control of quantum systems, so that is nowadays possible to manipulate with a high level of control small quantum systems.

The problem is then to infer what is the best protocol given some partial microscopic information on the system -the system will be generically represented by a density matrix, the entropy of which measures the level of ignorance.

A seminal work to deal with work extraction using general operations was developed by Pusz and Woronowicz in (PW78), see also the work of Lenard (Len78). In these works, the set of possible operations for work extraction consists of all unitary operations on the system of interest. Note that, in quantum physics, every evolution of a closed system can be described by a unitary operation. In turn, for every open system, a closed super-system can be constructed by considering the surrounding with which the system is interacting with. Hence the considered set of operations is remarkably large.

Within this set of operations, the concept of a passive state was introduced in (PW78) as those states from which no work can be extracted -conversely, non-passive states are those states which store work. Remarkably, passive states have the property of activation: when considered as a whole, several copies of passive states can become non-passive. The only states lacking this property are thermal, or Gibbs, states. This selects Gibbs states, which are also known as completely passive states, as the only states that are genuinely useless for work extraction: Even if one posses an infinite amount of Gibbs states (at the same temperature), no work can be extracted from them. Complete passivity of thermal states has motivated their role as free states in the recently introduced resource theory of thermodynamics (BaHO$^+$13).

An important observation in activation processes is that they can only be implemented via global operations -indeed, at the local level the states are passive and have no extractable work. The amount of work that can be extracted in the thermodynamic limit via such operations was recently studied in (AF13).

Motivated by these considerations, we develop two different projects on the phenomenon of activation. The first one is motivated by the fact that all all passive-but-not-thermal states contain some work that can be potentially activated. We study how large such an activable work can be, which allows us to find how energetically different are passive states from thermal states. The second main question arises from the observation that global unitary operations, which are necessary for activation, are also needed for generating entanglement. This motivates us to characterise the exact relation between entanglement and the extracted work.

Main results

The problem of finding the passive states with maximal actionable work turns out to be the same as maximising (minimising) the energy (entropy) for a given entropy (energy) within the set of passive states - note that Gibbs states provide the dual solution to such optimisations. The solution to this optimisations yields a one parameter family, which we term the most energetic passive states. This family can be seen as the dual of Gibbs states, where the free parameter plays the role of the temperature. This observation naturally allows us to obtain some fundamental bounds for work extraction for finite dimensional quantum systems. Furthermore, we quantify how energetically different are passive states from Gibbs states, finding strikingly different results depending on the structure of the Hamiltonian.

In a different project, we investigate in detail the activation process of passive states, in particular the role of entanglement. We show that, while all work can be extracted without generating entanglement at any point, entanglement can increase the *speed* of the process.

1.1.2. Second law of thermodynamics

State of the art and motivation

The concept of passive states appears when one considers work extraction from a system that is thermally isolated from its surroundings. Yet, thermodynamics is very much concerned with the situation where energy exchanges between the system and a surrounding thermal bath take place. Here we investigate a version of the second law, *the extractable work from a system is bounded by the free energy difference*, which is defined in this setting.

The scenario of (PW78; Len78) can be extended to account for a thermal bath by taking an initial state consisting of a system (out of equilibrium) and a thermal state. The allowed operations are then any unitary operation on the joined state. While formally correct, this is a rather theoretical approach: The thermal bath is macroscopic, with an enormously large number of degrees of freedom, and hence assuming controlled unitaries on the bath is impossible at the practical level. Even with this unrealistic level of control, recent results in the literature, see e.g. (EVdB11; BaHO^{+}13; SSP14), show that the second law of thermodynamics still holds true. This result is very remarkable because in order to saturate the bound given by the second law, no control over the bath is required: A weak interaction between system and bath is enough to bound the limit set by the second law (AG13; Abe13). Nevertheless, the bath must have some specific properties, in particular having infinite size and a continuous spectrum.

Motivated by these results, in our work we study situations where, even with unlimited control over the state of system and bath, saturating the second law is not possible due to the finite size of the bath or the lack of a continuous spectra.

Main results

Following (EVdB11; RW14), we derive an exact equality which holds for arbitrary unitary operations, from which the second law of thermodynamics follows. This expression permits us to identify the different sources of non-optimality in work extraction processes. We also construct explicit optimal protocols for work extraction that saturate the second law. These protocols require a continuous spectrum for the thermal bath, as well as an infinite size. By computing the maximal extractable work in absence of these properties, we find corrections to the second law arising from either finite size effects or the bath structure.

1.1.3. Fluctuations of work in quantum coherent processes

State of the art and motivation

Phenomenological thermodynamics is formulated as an exact set of relations among macroscopic quantities, such as heat and work. With the development of statistical physics, it was realised that thermodynamic variables could be interpreted as the average of (complex) microscopic magnitudes. For example, thermal energy can be associated with the statistical mean of the the kinetic energy of the systems' particles. Therefore, the laws of thermodynamics have a probabilistic nature: They are to be satisfied on average, but nothing prevents their violation for small periods of time, or in particular realisations of an experiment. The crucial realisation is that (usually) thermodynamics deals with extremely large systems where, because of the law of large numbers, the probability of observing noticeable divergences from the average value becomes zero for all practical purposes.

The situation changes drastically when we deal with mesoscopic systems, or even with systems of a few particles, as it is often done in quantum thermodynamics. In this case, fluctuations do become relevant, and their characterisation is important. In classical physics, relations to characterise the fluctuations in thermodynamic processes were developed in the form of fluctuation theorems (see (SPWS08; EHM09) for reviews on the topic). Fluctuation theorems are exact relations about the whole probability distribution, not only the average, of thermodynamic variables. They can quantify the probability of processes which are not necessarily allowed by the second law, but can occur with a small probability.

The celebrated Jarzyinsky fluctuation theorem (Jar97), which characterises the fluctuations of work, was extended to the quantum regime in (TLH07) (see also the recent review (HT15) and references therein). The result was based on a particular measurement scheme to estimate work, consisting of two measurements of energy, one done at the beginning and one at the end of the process. Work is then associated with the difference of energies of the results of the two measurements (TLH07). While this scheme successfully extends the fluctuation theorems to the quantum regime, it has an important drawback: It does not allow for a description of quantum coherent processes. Indeed, the first energy measurement destroys any energy coherence, and forces the system to behave as a classical state, with a well defined energy.

In our project we aim to extend the results of (TLH07) to states with quantum coherence, by devising new measurement schemes that have a smaller back action on the initial state.

Main results

By considering general measurement schemes to estimate the fluctuations of work, we first set fundamental limitations on the possibility of measuring work fluctuations in coherent processes. Then we devise new strategies which allow for the (approximate) characterisation of the fluctuations of work in coherent processes.

1.1.4. Extractable work from correlations

State of the art and motivation

One of the immediate consequences of the second law of thermodynamics is that there exists no cyclic process which extracts work from a thermal bath. Indeed, if it was possible, one could construct a *perpetuum mobile* machine, which would transform the dissipated heat into work with no additional cost.

The standard way to overcome this limitation is to obtain two thermal baths at different temperatures. Each bath is, by itself, completely useless; but the combination of both creates a heat flow that can be used for the extraction of work. In other words, the hot bath is not in thermal equilibrium with the cold one, and vice versa, and the corresponding absence of equilibrium is potentially useful energy, i.e., work. At the theoretical level, it is not difficult to imagine other origins for the work source. A seminal example is the Szilard engine, which uses *information* as a source to extract work (Szi29).

In our work we aim to investigate the potential of correlations as a source of work. For that, we consider a set of correlated systems that, at the individual level, are found at thermal equilibrium at the same temperature. Because of the result by (PW78), it follows that all the extractable work can only come from the correlations between the states. We then investigate how much work can be stored in such correlations, and whether this amount depends on the quantum nature of them.

Main results

We consider general entangled states, separable states, and correlated states with fixed global entropy. For each class of states, we find the optimal state for storing work and the corresponding protocol to extract it. Our results show that entanglement provides an advantage for work storage, although this advantage decreases as the number of correlated systems increases, vanishing in the thermodynamic limit.

1.1.5. Fundamental limitations for creating correlations in thermodynamic environments

State of the art and motivation

Quantum information protocols strongly rely on entanglement, which is the root of relevant applications in cryptography, metrology, or quantum computation. In order to obtain maximally entangled states, the state needs to be pure, i.e., one has perfect control and knowledge of it. Yet, in real applications, it is to be expected that noise will diminish the purity of the state. Here we are interested in understanding the limitations and possibilities for generating entanglement and correlations in thermal states at finite temperature.

The thermodynamic-like limitations that we consider for generating entanglement and correlations are of two types,

- limitations arising form the initial temperature, and
- limitations arising form the available energy.

Regarding the first type, in quantum information it is known that there are states that are too mixed to become entangled, i.e., there exists no unitary operation that can generate entanglement on them (GB02; GB03) (see also (HHHH09) for a review in entanglement theory). Hence, it is to be expected that states at high temperatures, which are very mixed, are useless for creating entanglement. Our aim is in fact to find what is the maximal temperature that allows for the generation of different forms of entanglement.

The second limitation that we consider is related to the work cost of generating entanglement and correlations. Since we consider states that are initially at thermal equilibrium, a positive amount of work needs to be invested in order to move them out of equilibrium and create correlations. The question is then what is the minimal work cost to generate a certain amount of correlations or entanglement.

Main results

We consider a set of independent thermal states at the same temperature, and consider the possibility of implementing any unitary operation on them. We find what is the maximal temperature allowing for the generation of different types of entanglement, which depends on the number of copies that are available. We show that even genuine multipartite entanglement -the strongest form of entanglement in multipartite systems- can be created at any temperature when sufficiently many systems are considered. We also investigate the work cost of producing entanglement and correlations by constructing explicit protocols for generating a unit of correlation or an e-bit (a fundamental unit of entanglement) at minimal energy cost.

1.1.6. Thermodynamics in the context of Generalized Gibbs Ensembles

State of the art and motivation

It has been stressed the fundamental role that Gibbs states play in thermodynamics, which was motivated because they are the only completely passive states. There is another very strong reason why Gibbs states are ubiquitous in thermodynamics: One expects that out of equilibrium systems will eventually relax to a thermal state. This can be roughly justified by the observation that (i) thermal states maximize the entropy, and (ii) according to the second law of thermodynamics the entropy of a closed system can only increase. Hence, it follows from (i) and (ii) that if the entropy increases continuously the final state must be a thermal state - the temperature of which is defined by the energy of the overall system. This is indeed what we observe in our daily life: For example, take two systems at different temperatures -and hence globally out of equilibrium- and after a sufficiently large time they will reach an equilibrium state well described by a thermal state at an intermediate temperature.

At the quantum level, equilibration and thermalisation are intense topics of research, and an unified picture is still missing (see (PSSV11; GE15) for reviews on equilibration and thermalisation in quantum systems). What is nevertheless widely accepted is that there exist systems which reach equilibration, but the corresponding equilibrium state is not well described by a thermal state. A relevant example are integrable models, the equilibrium states of which are given by the so called generalized Gibbs ensembles (GGE) (CDEO08; CCR11).

Our aim is to study relevant processes in thermodynamics, such as entropy production or work extraction, for equilibrium states that are well described by GGE states.

Main results

We consider three kinds of equilibration, namely to (i) the time averaged state, (ii) the generalised Gibbs ensemble (GGE) and (iii) the Gibbs ensemble. Those are three effective descriptions with decreasing detail of the equilibrium state (GE15). For each effective description, we investigate entropy production, the validity of the minimal work principle and properties of optimal work extraction protocols. As in phenomenological thermodynamics, we show that in infinitesimally slow protocols no entropy is generated in any of the equilibrium states, and are hence reversible. Reversible processes are also optimal processes for work extraction, a phenomenon which is referred to as the minimum work principle. We identify significant differences regarding the applicability of this principle for the different types of equilibration.

1.2. Outline of the thesis

This Thesis is organized as follows:

- Chapter 2 gives an introduction to basic concepts that appear through all the Thesis.
- Chapter 3 is devoted to the study of work extraction and passive states. This chapter is based on the following original results: (PLHH^{+}15b; HPLHA13).
- Chapter 4 is dedicated to the study of the second law of thermodynamics. The results are new and unpublished.[2]
- Chapter 5 contains our considerations on the fluctuations of work in quantum coherent processes. The results are new and unpublished.[3]
- In Chapter 6 the amount of extractable work from correlations is investigated. This chapter is based on the following original results: (PLHH^{+}15a). Sec 6.7 is original and not published.
- In Chapter 7 we study the generation of entanglement and correlations starting from thermal states. This chapter is based on the following original results: (HPLH^{+}15; BPLF^{+}15; FHPL).
- Chapter 8 contains our considerations about generalised Gibbs ensembles and thermodynamics. It is based on the following (unpublished) original results: (PLRG^{+}15).

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[2] These results arise through a collaboration with Paul Skrzypczyk and Karen Hovhannisyan. A prepint including these results is expected in the next few months.

[3] These results arise through a collaboration with Antonio Acín, Elisa Bäumer, Karen Hovhannisyan and Marcus Huber. A prepint including these results is expected in the next few months.

2. Preliminaries

In this Chapter we aim to give the basic tools and concepts used throughout this thesis. It has two main sections, one devoted to quantum thermodynamics and one to quantum information. Let us point out that specific background for certain results of this thesis will be presented at the beginning of the corresponding chapter.

2.1. Quantum thermodynamics

Thermodynamics provides us with laws governing the exchange of energy in form of work and heat. Nevertheless, in the quantum regime, the very definition of work is still a matter of debate (see e.g. (TLH07; SSP14; GEW15; Abe13) for different approaches to the definition of work in the quantum regime). Here we present a rather standard textbook definition (LL80; GMM09), and leave recent insights and alternative definitions of the concept of work for later points of this thesis.

2.1.1. Work, heat, and the first law of thermodynamics

Let us consider a quantum system $\rho(t)$ with an internal Hamiltonian $H(t)$. The (average) internal energy of the system at time t is simply given by,

$$E(t) = \mathrm{Tr}\left(\rho(t)H(t)\right). \tag{2.1}$$

This energy varies in time as the system exchanges energy in, qualitatively, two distinct ways,

- Work-like energy. This energy is associated with the variation of external parameters that can be controlled, such as volume. In the quantum case this corresponds to the change of the Hamiltonian H in time.

- Heat-like energy. This energy is associated with non-controlled energy exchanges of the system with its surroundings.

In order to quantify these two energic quantities, one defines work as

$$W = -\int_0^\tau dt \mathrm{Tr}\left(\rho(t)\frac{dH(t)}{dt}\right) \tag{2.2}$$

and the remaining energy is associated to heat,

$$Q = \int_0^\tau dt \mathrm{Tr}\left(\frac{d\rho(t)}{dt}H(t)\right). \tag{2.3}$$

Here we take the convention that work is extracted from the system, whereas heat is absorbed -that explains the minus sign. By construction, the first law of thermodynamics is satisfied,

$$\Delta E = Q - W \tag{2.4}$$

which is nothing but energy conservation.

It is important to note that work and heat are process dependent functions. This is seen here by the fact that they can not be computed as an instantaneous function of the couple $(\rho(t), H(t))$, as the average energy in (2.1), but rather depend on the whole time evolution- i.e., the path from $(\rho(0), H(0))$ to $(\rho(t), H(t))$. At the infinitesimal level, this implies that work and heat are in general not full differentials, and will be denoted as δW and δQ.

Example: A thermally isolated system

In order to gain a better understanding of these definitions, let us consider a thermally isolated system. In this case, the only variation of energy comes from the time dependent nature of $H(t)$,

$$H(t) = H + V(t). \tag{2.5}$$

The state ρ then evolves as,

$$i\hbar\frac{d\rho(t)}{dt} = [H(t), \rho(t)] \tag{2.6}$$

From (2.2), we obtain easily,

$$Q = \frac{1}{i\hbar}\int_0^\tau dt \mathrm{Tr}\left([H(t), \rho(t)]H(t)\right) = 0 \tag{2.7}$$

where we used the cyclic property of the trace. Hence,

$$W = \mathrm{Tr}(H(0)\rho) - \mathrm{Tr}(H(\tau)\rho(\tau)). \tag{2.8}$$

Summarizing, when the system is thermally isolated, there is no heat exchange, and work is equal to the change of internal energy.

2.1.2. Second law of thermodynamics

Assume now that the system is immersed in a thermal bath at temperature T. We introduce the thermodynamic entropy as the heat exchanged in a *reversible* process,

$$\Delta S_{\mathrm{th}} \equiv \int_{\mathrm{rev}} \frac{\delta Q}{T}. \tag{2.9}$$

The Clausius formulation of the second law of thermodynamics then states that,

$$\int \frac{\delta Q}{T} \leq \Delta S_{\mathrm{th}}. \tag{2.10}$$

That is, the change of the entropy of the system must be equal or larger than the average heat absorbed by the system during the process. If we now define the equilibrium free energy as,

$$F_{\mathrm{eq}}(\rho) = \mathrm{Tr}(H\rho) - TS_{\mathrm{th}}(\rho), \tag{2.11}$$

we obtain from (2.10) and the first law of thermodynamics,

$$W \leq -\Delta F_{\mathrm{eq}}. \tag{2.12}$$

That is, the extractable work from a system is bounded by the difference of free energies, an equivalent formulation of the second law.

In order to compute the thermodynamic entropy S_{th}, let us introduce the Von Neumann entropy,

$$S(\rho) = -\operatorname{Tr}\rho \ln \rho. \tag{2.13}$$

Then, for states in thermal equilibrium, i.e. states of the form,

$$\tau_\beta = \frac{e^{-\beta H}}{\mathcal{Z}} \tag{2.14}$$

where $\mathcal{Z} = \operatorname{Tr} e^{-\beta H}$, it is known that the thermodynamic entropy equals the Von Neumann entropy,

$$S_{\mathrm{th}}(\tau_\beta) = k_B S(\tau_\beta), \tag{2.15}$$

where k_B is the Boltzmann constant, which, from now one will take it to be equal to 1. This provides a simple recepy to compute the thermodynamic entropy for equilibrium states, which is in fact the regime where traditional thermodynamics applies.

Extending the definition of thermodynamic entropy for states out of equilibrium is a difficult problem even in the classical regime, and is still debated nowadays. A standard approach is to keep the relation (2.15), i.e., to define the out-of-equilibrium entropy of a state ρ as its Von Neumann entropy, (2.13). In this case, the non-equilibrium free energy is defined as,

$$F(\rho) = \mathrm{Tr}(H\rho) - TS(\rho), \tag{2.16}$$

which provides a more refined version of the second law (2.12). In Chapter 4, we will discuss in detail this form of the second law, and show that (2.16) provides a meaningful way to extend the second law (2.12) for out of equilibrium processes.

2.1.3. Work extraction and passive states

Let us now study the problem of work extraction from quantum systems in more detail. We focus on processes where the system is thermally isolated, so that no heat is exchanged at any point during the process (extensions including thermal environments will be discussed in Chapter 4). We also consider cyclic processes, in the sense that the Hamiltonian is the same at the beginning and at the end of the process.[1]

Cyclic Hamiltonian processes can be described by a time dependent field $V(t)$, which is being turned on during a time interval $t \in [0, \tau]$. Since the system is thermally isolated, the evolution of ρ can be described by a unitary operator

$$U(\tau) = \overrightarrow{\exp}\left(-i\int_0^\tau dt\,(H + V(t))\right), \tag{2.17}$$

where $\overrightarrow{\exp}$ denotes the time-ordered exponential. By appropriately choosing $V(t)$ we can generate every unitary operation $U = U(\tau)$, and thus the operations considered in this context are essentially all unitary operations.

Note that this scenario is the same as the one discussed in Sec. 2.1.1. Therefore, the extracted work W is given by

$$W = \mathrm{Tr}\,(\rho H) - \mathrm{Tr}\left(U\rho U^\dagger H\right). \tag{2.18}$$

where we used that $V(0) = V(\tau) = 0$. The internal (time-independent) Hamiltonian of the system can be decomposed as,

$$H = \sum_i e_i |i\rangle\langle i| \quad \text{with} \quad e_{i+1} \geq e_i. \tag{2.19}$$

---

[1] Note that cyclicity is essential, otherwise the problem of work extraction becomes trivial: If any transformation of the Hamiltonian H can be performed, one can extract an arbitrary amount of work by adding negative terms to H, so that the system loses (an arbitrary amount of) energy.

Within the definition (6.3), work can be extracted from a system if and only if the system is *non-passive*, where a passive system has the form (PW78; Len78),

$$\sigma_p = \sum_i p_i |i\rangle\langle i|, \quad \text{with} \quad p_{i+1} \leq p_i. \tag{2.20}$$

That is, passive states are diagonal in the energy basis and do not have population inversions (PW78; Len78). We now prove this result following (Len78). Let U be a unitary operation and σ_p be a passive state, then

$$\mathrm{Tr}\left(HU\sigma_p U^\dagger\right) = \sum_k p_k e_k |\langle k|U|k\rangle|^2 \geq \sum_k p_k e_k = \mathrm{Tr}\left(H\sigma_p\right) \tag{2.21}$$

where we used the fact that $|\langle k|U|k\rangle|^2$ is a probability distribution and that $\{p_k\}$ are decreasingly ordered. That is, any unitary acting on σ_p can only increase its energy; and hence no work can be extracted from it. It easily follows that, given a non-passive state ρ, the extracted work (6.3) is maximised by (ABN04),

$$W_{\max} = \mathrm{Tr}(\rho H) - \mathrm{Tr}(\rho^{\text{passive}} H) \tag{2.22}$$

where ρ and ρ^{passive} are related through a unitary transformation (ρ^{passive} has the form (2.20) with the p_i's given by the spectrum of ρ).

2.1.4. Activation, complete passivity, and Gibbs states

An interesting scenario appears when we consider the possibility to process several copies of a passive state, i.e.,

$$\rho = \otimes^n \sigma_p. \tag{2.23}$$

Here the Hamiltonian is simply given by the sum of local Hamiltonians, $H^{(T)} = \sum_i H^{(i)}$. As n increases, population inversions can start appearing in ρ, which hence becomes non-passive. This is easily illustrated by an example. Consider two identical 3-level systems σ_p in a passive state, with

$$h^{(i)} = \mathrm{diag}\{e_0, e_1, e_2\} \tag{2.24}$$

and

$$\sigma_p = \mathrm{diag}\{p_0, p_1, p_2\} \tag{2.25}$$

where $p_0 \geq p_1 \geq p_2$. Suppose now that $p_o p_2 > p_1^2$ while $e_0 + e_2 > 2e_1$. The state $\sigma_p^{\otimes 2}$ is non-passive, as a population inversion appears among the levels $e_0 + e_2$ and $2e_1$. Hence a (global) unitary operation exchanging these two levels can extract work from the state.

Remarkably, it can be shown that if n is sufficiently large, population inversions always start appearing in $\otimes^n \sigma_p$, the only exception being Gibbs or thermal states (PW78; Len78). The fact that Gibbs states are the only non-activable states will be proven in Chapter 3 following Ref. (AF13). Here, we just note that Gibbs states keep their structure under composition,

$$\bigotimes_i \frac{e^{-\beta H^{(i)}}}{\mathcal{Z}_i} = \frac{e^{-\beta H^{(T)}}}{\mathcal{Z}} \tag{2.26}$$

where $\mathcal{Z} = \prod_i \mathcal{Z}_i$, and hence they remain passive, no matter how many copies one considers. This is why they are also referred to as *completely passive states*.

As a final remark we note that connections between passivity, free energy, and the second law of thermodynamics will be provided in Chapter 4.

2.2. Quantum Correlations

Let us now turn to quantum information theory. A big part of this thesis is related to the connection between thermodynamics and correlations. Particular emphasis will be put in entanglement, a form of correlations that only exists in the quantum world.

2.2.1. Correlations

Consider a bipartite quantum state ρ_{AB}. Correlations between the two systems (denoted by A and B) can naturally be measured using the quantum mutual information I_{AB},

$$I_{AB} = S(\rho_A) + S(\rho_B) - S(\rho_{AB}), \tag{2.27}$$

where $\rho_{A,B} = \mathrm{Tr}_{B,A}\, \rho_{AB}$ and $S()$ is the Von Neumann entropy. Note that, iff A and B are independent, i.e., $\rho_{AB} = \rho_A \otimes \rho_B$, then $I_{AB} = 0$.

In the multipartite setting one can generalise the notion of mutual information by considering the difference between the sum of local entropies and the total entropy of the system. That is, for a collection of n subsystems

$A_1, \ldots, A_n$, we define the multipartite mutual information as

$$I_{1\ldots n} = \sum_{i=1}^{n} S(\rho_i) - S(\rho), \tag{2.28}$$

where ρ_i is the local state of subsystem A_i. This quantity vanishes only when the total system is a direct product.

2.2.2. Entanglement

Entanglement is a direct consequence of the linearity of quantum mechanics and the composite structure of Hilbert spaces. While it is hence a very natural phenomena in quantum physics, it has no classical counterpart. This gives to entanglement a unique status: It is at the core of some the most amazing properties of quantum physics, such as Bell non-locality, and at the is same responsible for many applications of quantum information and computation.

In order to define entanglement, consider an bipartite pure state $|\phi_{AB}\rangle$. We say $|\phi_{AB}\rangle$ is entangled if it *cannot* be written as a tensor product,

$$|\phi_{AB}\rangle \neq |\phi_A\rangle \otimes |\phi_B\rangle. \tag{2.29}$$

Otherwise, the state is separable. This notion is extended to mixed states as follows: A density matrix ρ is said to be entangled if it *cannot* be written as a convex combination of pure separable states,

$$\rho \neq \sum_i p_i |\phi_A^{(i)}\rangle\langle\phi_A^{(i)}| \otimes |\phi_B^{(i)}\rangle\langle\phi_B^{(i)}|. \tag{2.30}$$

We note that this definition of entanglement comes from the observation that states of the form (2.30) can be generated by local operations and classical communication (NC00).

In order to appreciate the power of entanglement, let us consider a two qudit system, i.e. two d-level systems, and the following entangled state,

$$|\psi\rangle = \sum_i \frac{1}{\sqrt{d}} |ii\rangle. \tag{2.31}$$

If we compute the mutual information of this state, we obtain,

$$I_{AB}^{(\psi)} = 2 \ln d. \tag{2.32}$$

This is in fact the maximum of I_{AB}, as the Von Neumann entropy of a d-dimensional system is upper bounded by $\ln d$. Hence, we see that the correlations of $|\psi\rangle$ are maximally strong. Not only that, but if we now consider separable states, one finds that (NC00),

$$I_{AB}^{\text{sep}} \leq \ln d. \tag{2.33}$$

That is, the strength of the correlations in entangled states can be twice as much as in separable states.

The quantification and detection of entanglement is known to be a hard task. The standard measure of entanglement for pure states is the *entropy of entanglement*,

$$\mathcal{E}(|\psi_{AB}\rangle) = S(\rho_A) = S(\rho_B) \tag{2.34}$$

where $S(\rho)$ is the Von Neumann entropy. This measure can be extended to mixed states via the convex-roof construction

$$\mathcal{E}(\rho) = \inf \sum_i p_i \mathcal{E}(\psi_i), \tag{2.35}$$

where the infimum is taken over all pure state decompositions $\rho = \sum_i p_i |\psi_i\rangle\langle\psi_i|$. This measures is known as *entanglement of formation*. The difficulty of computing/detecting entanglement lies in the minimization in (2.35). Several alternative measures of entanglement, such as the entanglement negativity, have also been proposed (see Ref. (HHHH09) for a review in entanglement theory). Those measures cannot detect all entangled states but can be efficiently computed.

The situation is simpler in the case of bipartite qubit systems, where the entanglement of formation can be analytically computed. For that, one defines the *concurrence* (Woo98) which, for pure states, is the linear entropy of the reduced state of one party,

$$\mathcal{C}(\psi) = \sqrt{2(1 - \mathrm{Tr}(\rho_{\mathrm{A}}^2))}, \tag{2.36}$$

where $\rho_{\mathrm{A}} = \mathrm{Tr}_{\mathrm{B}}|\psi\rangle\langle\psi|_{\mathrm{AB}}$. This measure can be indeed functionally related to the entropy of entanglement. Again, the definition (2.36) can be extended to mixed states via the convex-roof construction $\mathcal{C}(\rho) = \inf \sum_i p_i \mathcal{C}(\psi_i)$. For qubit systems, the convex roof can be analytically calculated, yielding (Woo98)

$$\mathcal{C}(\rho) = \max(0, \lambda_1 - \lambda_2 - \lambda_3 - \lambda_4) \tag{2.37}$$

in which $\lambda_1, ..., \lambda_4$ are the eigenvalues, in decreasing order, of the Hermitian matrix

$$R = \sqrt{\sqrt{\rho}\tilde{\rho}\sqrt{\rho}} \tag{2.38}$$

with

$$\tilde{\rho} = (\sigma_y \otimes \sigma_y)\rho^*(\sigma_y \otimes \sigma_y). \tag{2.39}$$

Multipartite setting

The previous measures can be naturally extended to multipartite systems. Here, states can be *fully separable*, *partially entangled*, or *genuinely multipartite entangled*.

The level of entanglement in multipartite states can be quantified by introducing the notion of k-separability. An n-partite pure quantum state $|\phi_{\mathrm{ksep}}\rangle$ is called k-separable, if it can be written as a product of k states:

$$|\phi_{\mathrm{ksep}}\rangle = |\phi_1\rangle \otimes |\phi_2\rangle \otimes \ldots \otimes |\phi_k\rangle \tag{2.40}$$

A mixed state ρ_{ksep} is called k-separable, if it has a decomposition into k-separable pure states,

$$\rho_{ksep} = \sum_i p_i |\phi_{\mathrm{ksep}}\rangle\langle\phi_{\mathrm{ksep}}|. \tag{2.41}$$

Particularly relevant are the two extreme cases: A n-partite state is called fully separable if it is n-separable; and it is called genuinely multipartite partite entangled (GME) if it is 1-separable.

In the multipartite setting, a state can be entangled in many inequivalent ways, which do not only depend on the number of parties involved in the entanglement (e.g., there are different classes of GME entangled states). To understand this idea, consider first the case of two qubits. The maximally entangled state, also known as an Einstein-Podolsky-Rosen (EPR) pair, reads

$$|\phi\rangle = \frac{1}{\sqrt{2}}(|00\rangle + |11\rangle). \tag{2.42}$$

There is a deep reason why the EPR pair is the most powerful entangled state, besides the fact that it maximizes the entanglement measures defined above. Consider the set of LOCC operations, i.e., operations consisting of local operations and classical communication. By the very definition of separability in (2.30), every separable state can be constructed with LOCC operations, but no entanglement can be generated with them -in fact LOCC can only decrease the amount of entanglement. Now, given an EPR pair, one can deterministically obtain any pure state using only LOCC operations (Nie99). Conversely, an EPR state can be probabilistically obtained from any bipartite qubit entangled state using SLOCC (stochastic LOCC).

This result gives a unique status to the EPR pair, being the optimal resource for constructing states in terms of LOCC operations. The uniqueness of a maximally entangled state is lost in the multipartite setting. That is, there is no single state from which any state can be obtained, even probabilistically. Convertibility among states via LOCC and SLOCC operations have extensively studied in the multipartite setting (see the recent results in (SSC$^+$15) and references therein). For three qubits, it is known that there are two inequivalent classes of entangled states, which are given by,

$$\begin{aligned} |\phi_{\mathrm{GHZ}}\rangle &= \frac{1}{\sqrt{2}}(|000\rangle + |111\rangle) \\ |\phi_{\mathrm{W}}\rangle &= \frac{1}{\sqrt{3}}(|001\rangle + |010\rangle + |100\rangle). \end{aligned} \tag{2.43}$$

Each of these states is a different resource, as the states they can generate via (S)LOCC operations have no overlap. Both the GHZ and the W are widely used in quantum information. They can be easily extended to the multipartite setting, although in this setting many more inequivalent entanglement classes appear, and its characterization depends on the framework one uses (see e.g. (SSC$^+$15) for a recent discussion).

3. Work extraction from thermally isolated systems

This chapter is devoted to the study of passive states, with special attention to the phenomenon of activation. In Sec. 3.1, we start by presenting the seminal result of (PW78; Len78), namely that all passive states can be activated in the thermodynamic limit (i.e. when an arbitrary large amount of copies are processed) except for Gibbs states. Following (AF13), in this section we also compute what is the extractable work in this limit, which is given by the difference of free energies. Next, in Sec. 3.2, we present our first original contribution, namely finding the most energetic passive states, which gives an upper bound to such an extractable work. Finally, Sec. 3.3 is devoted to the study of the role of entanglement in activation processes, and our main contribution is to show that entanglement can increase the speed of such processes.

3.1. Maximal extractable work in the thermodynamic limit

This section is based on the results of (AF13). The main goal is to compute how much work can be extracted from,

$$\rho = \otimes^n \sigma_p \tag{3.1}$$

in the asymptotic limit $n \to \infty$, where σ_p is a passive state. For that, let us first bound the extractable work (2.22). By noting that (i) unitary transformations preserve the Von Neumann entropy, and that (ii) for a fixed entropy, Gibbs state are the states minimising the average energy, we have that,

$$\mathrm{Tr}(\rho H) \geq \mathrm{Tr}(\rho^{\mathrm{passive}} H) \geq \mathrm{Tr}(\tau_{\beta'} H) \tag{3.2}$$

where $\tau_{\beta'}$ is a fictitious Gibbs state whose temperature β' is chosen such that $S(\rho) = S(\tau_{\beta'})$ is satisfied. Using (3.2) we immediately arrive at a bound for the maximum extractable work from ρ,

$$W_{\max} \leq \mathrm{Tr}(\rho H) - \mathrm{Tr}(\tau_{\beta'} H). \tag{3.3}$$

In the single copy case, this bound can only be reached if ρ and $\tau_{\beta'}$ have the same spectrum. Remarkably, this bound can be reached in the asymptotic limit $n \to \infty$, in the sense that the total $W_{\max}$ divided by n tends to the right hand side of (3.3) (AF13). Let us now sketch the proof of this result, which is based on typicality arguments.

Let $\sigma_p = \text{diag}\{p_1, ..., p_d\}$ and $h_j = \sum_{i=1}^{d} \epsilon_i |i_j\rangle\langle i_j|$ be the internal Hamiltonian of each system. Let us denote by $\mathbf{i} = i_1 \cdots i_n$ an n-bit string, with $|\mathbf{i}| = \sum_k i_k$. The states

$$|\mathbf{i}\rangle = |i_1\rangle \cdots |i_n\rangle \tag{3.4}$$

run over all d^n energy eigenstates of the total Hamiltonian $H^{(T)}$. Now, the vast majority of the population of $\sigma_p^{\otimes n}$ is located in the ϵ-*typical* subspace (see, e.g., (NC00)), which is that spanned by $|\mathbf{i}\rangle$'s of the form,

$$|\,\overbrace{0...0}^{(p_0+\epsilon_0)N}\,\underbrace{1...1}_{(p_1+\epsilon_1)N}\,...\,\overbrace{d...d}^{(p_d+\epsilon_d)N}\,\rangle, \quad \text{with} \quad |\epsilon_k| \leq \epsilon, \quad \sum_{k=1}^{d} \epsilon_k = 0$$

or any permutation of the indices. There are $e^{nS(\rho)}$ of such typical configurations, and they have probability

$$\prod_{k=1}^{d} p_k^{Np_k} \prod_{k=1}^{d} p_k^{N\epsilon_k}, \qquad |\epsilon_k| \leq \epsilon, \qquad \sum_{k=1}^{d} \epsilon_k = 0. \tag{3.5}$$

Note that for $n \to \infty$, ϵ can be chosen to be arbitrarily small with $\epsilon > 0$ (NC00). Thus the choice of $\{\epsilon_k\}$ slightly modifies the value of each probability.

Now we can use an identical argument to show that $\tau_{\beta'}^{\otimes n}$, for n large enough, can be well approximated by considering only the $e^{nS(\tau_{\beta'})}$ typical configurations. The key point is that, since $S(\tau_{\beta'}) = S(\sigma_p)$, there are the same numbers of typical configurations in $\tau_{\beta'}^{\otimes n}$ than in $\sigma_p^{\otimes n}$. Hence we can construct a unitary U^* that exchanges each typical state of $\tau_{\beta'}^{\otimes n}$ with each one of $\sigma_p^{\otimes n}$. Note that this transformation is highly degenerate. After the transformation the state $\sigma_p^{\otimes n}$ has the energy of $\tau_{\beta'}^{\otimes n}$ up to an exponentially small correction with n, and hence we obtain that the extracted work per copy, W^*, reads

$$\begin{aligned} W^* &= \lim_{n\to\infty} \frac{1}{n} \left(\text{Tr}\left(\sigma_p^{\otimes n} H^{(T)}\right) - \text{Tr}\left(U^* \sigma_p^{\otimes n} U^{*\dagger} H^{(T)}\right)\right) \\ &= \text{Tr}(\sigma_p H) - \text{Tr}(\tau_{\beta'} H) \end{aligned} \tag{3.6}$$

which saturates the bound (3.3).

3.2. The most energetic passive states

Our previous considerations have singled out *Gibbs states* among all passive states. In the single-copy case, Gibbs states provide a upper bound on the extractable work (3.3), and on the many-copies scenario they are the only ones that cannot be activated. Both of these results are essentially a consequence of the well known fact that Gibbs states maximize the entropy for a given energy, and similarly they minimize the energy for a given entropy. This naturally renders the question of what are the passive states lying in the other extreme, i.e., those which maximize the energy for a given entropy, and similarly minimize the entropy for a given energy.[1] Besides the genuine mathematical interest of this question, it is also clearly physically motivated, as the outcome of this optimization will bring a bound akin to (3.3) in the single copy case; and will allow us to quantify the maximal amount of work that can be potentially activated.

The results of this section are original and based upon (PLHH$^+$15b).

3.2.1. Main result

In this section, for a given entropy S and d-dimensional Hamiltonian H,

$$H = \sum_i e_i |i\rangle\langle i|, \tag{3.7}$$

we find the passive state that maximises the energy, which we denote by σ_p^*. It is convenient to first consider the complementary optimization, i.e., to find the passive state that minimizes the entropy for a fixed energy E. We will then show that both optimizations provide the same state.

Let us introduce the following set of d linearly independent states:

$$\omega_k = \frac{1}{k} \sum_{i=1}^{k} |i\rangle\langle i|. \tag{3.8}$$

Note that all states ω_k are passive and have the same spectrum of a microcanonical state (this distribution is known as the θ-canonical distribution). It is easy to see that any passive state can be written as a convex combination of such states,

$$\sigma_p = \sum_{i=1}^{d} q_i \omega_i, \tag{3.9}$$

---

[1] Note that it is important that the optimisations are carried out restricted to the set of passive states. Otherwise they become trivial: the state with the least entropy for a fixed energy is a pure state, and the state with the most energy for a fixed entropy is a thermal state with a negative temperature.

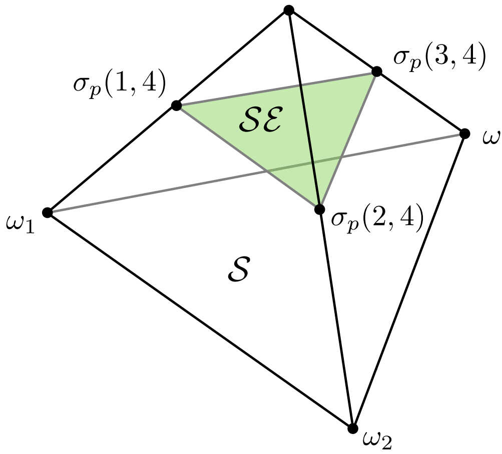

Figure 3.1.: Illustration of the set of all passive states $\mathcal{S}$ and the intersection with the constant energy hyperplane $\mathcal{SE}$ for a four dimensional system.

with $q_i \geq 0$ and $\sum_i q_i = 1$. This shows that the set of passive states defines a convex polytope, whose vertices are given by ω_k in (3.8). In fact the polytope is a simplex, i.e., any two vertices are connected by an edge. We denote the simplex spanned by all passive states as $\mathcal{S}$.

Within $\mathcal{S}$, we are interested in the subset of states with constant energy, $\mathrm{Tr}(\rho H) = E$. Since the energy $\mathrm{Tr}(\rho H)$ is a linear function, the condition $\mathrm{Tr}(\rho H) = E$ defines an hyperplane which intersects with $\mathcal{S}$. We denote by $\mathcal{SE}$ the polytope formed by this intersection, i.e.,

$$\mathcal{SE} = \{\sigma_p \;:\; \sigma_p \in \mathcal{S} \text{ and } \mathrm{Tr}(H\sigma) = E\}. \tag{3.10}$$

The point then is to minimize the entropy function $S(\sigma) = -\mathrm{Tr}(\sigma \ln \sigma)$ over $\mathcal{SE}$. These considerations are illustrated in Fig. 3.1.

Now, $\mathcal{SE}$ is a polytope and the entropy is a concave function, and, as is known from standard convex analysis, the minimum of a concave function over a polytope is achieved at one of its vertices. The vertices of $\mathcal{SE}$ have a simple form. They occur at the intersections of the energy hyperplane with the edges of $\mathcal{S}$ and therefore can be written as,

$$\sigma_p(k,l) = \lambda\omega_k + (1-\lambda)\omega_l \tag{3.11}$$

where $\lambda = \lambda(k,l)$ is determined from the energy condition:

$$\mathrm{Tr}(\sigma_p(k,l)H) = E, \tag{3.12}$$

which leads to,

$$\lambda(k,l) = \frac{\mathrm{Tr}(H\omega_l) - E}{\mathrm{Tr}(H\omega_l) - \mathrm{Tr}(H\omega_k)}. \tag{3.13}$$

Note that for consistency $\mathrm{Tr}(H\omega_k) \leq E \leq \mathrm{Tr}(H\omega_l)$ must be satisfied, i.e. the vertices must be separated by the energy hyperplane. In general, the set of feasible index pairs $\mathcal{I} = \{(k,l)|\mathrm{Tr}(H\omega_k) \leq E \leq \mathrm{Tr}(H\omega_l)\}$ depends on the spectrum of the Hamiltonian and the average energy E. It is however efficient to compute, with a system of dimension d requiring only to check $O(d^2)$ pairs. The last step of the optimization is to minimize the entropy over all feasible pairs

$$\sigma_p^* = \min_{\mathcal{I}} \sigma_p(k,l), \tag{3.14}$$

which can again be carried out efficiently for finite dimensional systems. We denote the solution as $\sigma_p^{\min}(E)$, and its entropy as $S_{\min}(E) \equiv S(\sigma_p^{\min}(E))$.

If $S_{\min}(E)$ is a monotonically increasing function of E, then $\sigma_p^{\min}(E)$ is also a solution of the complementary optimization, namely maximizing the energy when the entropy is fixed. In the following we show that this is the case by *reductio ad absurdum*. To proceed, let us define the polytope of all passive states with an energy greater than or equal to E,

$$\mathcal{SE}^+(E) = \{\sigma_p \ : \ \sigma_p \in \mathcal{S} \text{ and } \mathrm{Tr}(H\sigma) \geq E\}. \tag{3.15}$$

The vertices of this polytope are those of $\mathcal{SE}$ plus those vertices of $\mathcal{S}$ whose energies are at least E. Recall that, as it was used before, the minimum of $S(\sigma)$ over $\mathcal{SE}^+(E)$, $S^+_{\min}(E)$, is achieved on one of the vertices. Assume that it is one of the ω_k with $\mathrm{Tr}(H\omega_k) > E$. Consider the passive state $\alpha\omega_1 + (1-\alpha)\omega_k$, with λ given by $\lambda(k,1)$ in (3.13), so that its energy is equal to E. A direct calculation shows that $S(\alpha\omega_1 + (1-\alpha)\omega_k) < S(\omega_k)$, which contradicts our previous assumption. This implies that the minimum of $S(\sigma)$ over $\mathcal{SE}^+$ is attained on $\mathcal{SE}$, which, along with the observation that $\mathcal{SE}^+(E') \subset \mathcal{SE}^+(E)$ if $E' > E$, shows that the entropy is a non-increasing function of E.

In conclusion, the passive states that maximize the energy for a fixed entropy, and at the same time minimize the entropy for a given energy, are the one parameter family defined by (3.11). This family lies in the boundary of the set of passive states (see figure 3.2), which are convex combinations of states given by (3.8). This suggests a beautiful relation within the set of passive states between canonical and θ-canonical distributions: they give rise to the most and least stable states, respectively.

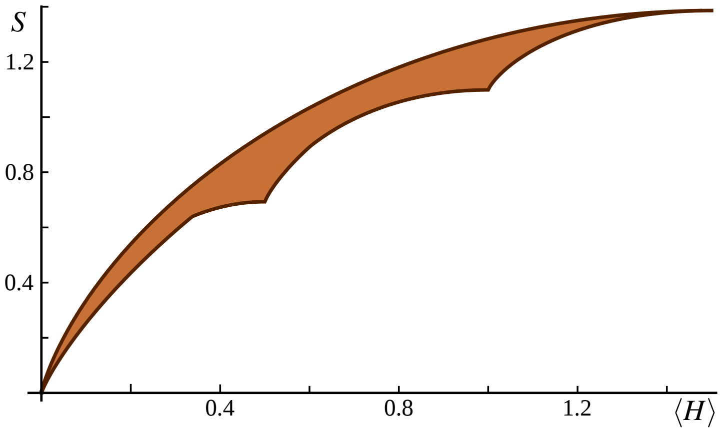

Figure 3.2.: Entropy versus energy for passive states given an equally spaced Hamiltonian of 4 levels, i.e., $H = \text{diag}\{0, 1, 2, 3\}$. The shaded area corresponds to the simplex $\mathcal{S}$. The two boundary curves correspond to the set of thermal states (upper) and the set of most energetic passive states (lower), obtained through (3.14).

3.2.2. Implications

In the single copy level, the main implication of σ_p^* is that it yields a lower bound on the maximal extractable work W_{max} from ρ, which is analogous to the upper bound (3.3). Explicitly, we obtain that

$$\text{Tr}(\rho H) - \text{Tr}(\sigma_p^* H) \leq W_{\text{max}} \leq \text{Tr}(\rho H) - \text{Tr}(\tau_{\beta'} H) \tag{3.16}$$

where $S(\sigma_p^*) = S(\rho) = S(\tau_{\beta'})$. Note that these bounds depend only on the entropy and the energy of ρ. That is, they allow to estimate the extractable work from ρ based only on global properties, as we expect from standard thermodynamic theories. In fact, if we accept that the Von Neumann entropy is the right generalization of the thermodynamic entropy for non-equilibrium states, then these bounds provide fundamental limitations on the extractable work from ρ based only on thermodynamic variables (energy and entropy).

In the many copy case, where one considers the possibility of extracting work from many copies of a passive state, the relation (3.6) clearly shows that σ_p^* is the state with the maximal amount of activable work. This is easy to understand because in the thermodynamic limit discussed in Sec. 3.1, the extractable work depends only on the initial energy and entropy of ρ. Therefore, if the minimal amount of work is extracted in the single-copy level (which corresponds to the case where the passive state associated to ρ is σ_p^*), then the amount of work extracted through activation must be maximal.

It is of course natural to wonder how these bounds behave for Hamiltonians that naturally occur in nature. For this purpose, in the next section we will study the behaviour of

$$\Delta_{\max}(S, E_p^*) = \mathrm{Tr}\left(H\sigma_p^*\right) - \mathrm{Tr}\left(H\tau_{\beta'}\right), \tag{3.17}$$

which quantifies the difference of energy between the least and most energetic passive states for a given entropy. This quantity also represents the locked work in σ_p^*.

3.2.3. Spectrum

The quantity $\Delta_{\max}(S, E_p^*)$ highly depends on the structure of H and its dimension. As an extreme case, when the dimension d of the system is 2, all passive states are thermal and thus $\Delta_{\max}(S, E_p^*) = 0$. As the dimension increases, so does $\Delta_{\max}(S, E_p^*)$, with a rate defined by the structure of H. In this section we give some general considerations in the limit of $d \to \infty$. These asymptotic results are then illustrated by exactly solving some specific systems for finite dimensions.

Our considerations strongly depend on the density of states (DOS), $g_{_E}$, which quantifies the number of states for energy level (the degeneracy). Indeed, the total number of states up to energy E, denoted as $N_{_E}$, is given by,

$$N_{_E} = \int_0^E dE' g_{_E}' \tag{3.18}$$

Typical Hamiltonians, e.g. those occurring in short-range interacting systems, have an exponential DOS. Roughly speaking, this can be justified by first assuming that entropy and energy are linearly related in macroscopic systems, as they are extensive variables; and second by assuming that $S_{_E} \approx \ln(N_{_E})$ at sufficiently large temperatures. These two natural assumptions are only compatible with an exponential DOS, $g_{_E} = e^{bE}$. Yet, long-range interacting systems, or simply few-body Hamiltonians, might very well have a DOS that grows substantially different. We now discuss the behaviour of $\Delta_{\max}(S, E_p^*)$ for DOS that grows either subexponentially or exponentially.

Polynomial growth of the density of states with energy.

Let us assume a dense spectrum bounded from above by E_m (the ground state is taken to be non-degenerate and to have zero energy). Assume first that the density of states (DOS) scales polynomially with energy,

$$g_E = cE^a, \tag{3.19}$$

where c is some positive constant. The total number of states within $[0, E]$ is then given by

$$N_E = \int_0^E dE' g_{E'} = \frac{c}{a+1} E^{1+a}. \tag{3.20}$$

Let us define ω_E as a state that is filled up to energy E, i.e., $\omega_E \equiv \omega_{N_E}$ in (3.8). It satisfies

$$\begin{aligned} \mathrm{Tr}[\omega_E H] &= \frac{1}{N_E} \int_0^E dE' g_{E'} E' = \frac{a+1}{a+2} E \\ S(\omega_E) &= \ln N_E . \end{aligned} \tag{3.21}$$

The MEPS is a combination of two such states, $\sigma_p^* = \lambda \omega_{E_1} + (1-\lambda)\omega_{E_2}$, with E_1, E_2 depending on the specific case (entropy of the state, spectrum, etc). Numerical analysis provides us with strong evidence that $E_1 = 0$ and $E_2 = E_\mathrm{m}$ is always the optimal choice for $N_E \gg 1$. Therefore we focus on

$$\sigma_0 = (1-\lambda)|0\rangle\langle 0| + \lambda \omega_{E_\mathrm{m}}, \tag{3.22}$$

where λ is determined by the energy (or entropy) of σ_0.

The energy and entropy of σ_0 can be straightforwardly computed, yielding

$$\begin{aligned} E(\sigma_0) &= \mathrm{Tr}[\sigma_0 H] = \lambda \frac{a+1}{a+2} E_\mathrm{m} \\ S(\sigma_0) &= H(\lambda) + \lambda \ln N_{E_\mathrm{m}} + O\left(N_{E_\mathrm{m}}^{-1}\right), \end{aligned} \tag{3.23}$$

where $H(\lambda) = -\lambda \ln \lambda - (1-\lambda)\ln(1-\lambda)$ is the binary entropy in natural units of information. From $E(\sigma_0)$ and $S(\sigma_0)$, one can express the entropy as a function of the energy, $S(E)$. In particular, we obtain that,

$$S(E) \to 0 \quad \text{for} \quad \frac{\ln \mathrm{E_m}}{\mathrm{E_m}} \mathrm{E} \to 0. \tag{3.24}$$

This relation implies that, if the norm of the Hamiltonian, E_m, is big enough, then essentially the state has zero entropy while having a finite energy. This is in sharp contrast with a thermal state, where if $S \to 0$ then $E \to 0$. On the other hand, this observation also implies that the work locked in a passive state $\Delta_\mathrm{max}(S, E_p^*)$ can be arbitrarily large if $E_m \to \infty$, which we can expect in the limit $d \to \infty$.

In order to illustrate these results, we consider an equally spaced Hamiltonian,

$$H = \epsilon \sum_{k=1}^{d} k|k\rangle\langle k|. \tag{3.25}$$

Of course, this Hamiltonian is naturally found in single-body systems, as in a harmonic oscillator, but is hardly imaginable in an interacting system. Note that, in this case, g_E is a constant, and the norm of the Hamiltonian increases linearly with the dimension, $E_m = Ed$. We have computed $\Delta_{\max}(S, E_p^*)$ as a function of d and S in Fig. 3.3, case (a). The figure (see especially the inset) shows how $\Delta_{\max}(S, E_p^*)$ increases linearly with d. Therefore, if the dimension is large enough, passive states have a large range of energies for a fixed entropy. In other words, there is a big energy gap, which increases with d, between the most and least energetic passive states. In the next section we will see that this gap dramatically shrinks for exponential density of states.

Bath-like spectrum

Assume now that the DOS now scales as

$$g_E = e^{bE}. \tag{3.26}$$

In this case, we again find strong numerical evidence that σ_0, as defined in (3.22), is the MEPS. After an straightforward computation we obtain,

$$\begin{aligned} E(\sigma_0) &= \lambda\left(E_m - b^{-1}\right) + O\left(e^{-bE_m}\right) \\ S(\sigma_0) &= H(\lambda) + \lambda \ln N_{E_\mathrm{m}} + O\left(N_{E_\mathrm{m}}^{-1}\right), \end{aligned} \tag{3.27}$$

From the expression of E we can determine $\lambda(E)$ which, together with $N_E = (e^{bE_m} - 1)/b$, can be inserted into $S(\sigma_0)$ to calculate $S(E)$. Taking, again, the limit $E/E_m \to 0$, we find in this case $S \to bE$. Therefore, we find that any amount of energy of the MEPS has an associated amount of entropy, even if the Hamiltonian is unbounded from above. Not only that, but if the energy is extensive -which is expected in a system of weakly interacting particles- so will be the entropy, as they are linearly related. This is exactly the behaviour found in thermal states. Hence, at least qualitatively, the most and least energetic passive states behave identically for an exponential growth of the DOS. We now confirm this observation quantitatively in a particular system.

We consider a collection of n non-interacting two-level systems,

$$H^{(T)} = \epsilon \sum_{i=1}^{n} \sigma_z^{(i)}, \tag{3.28}$$

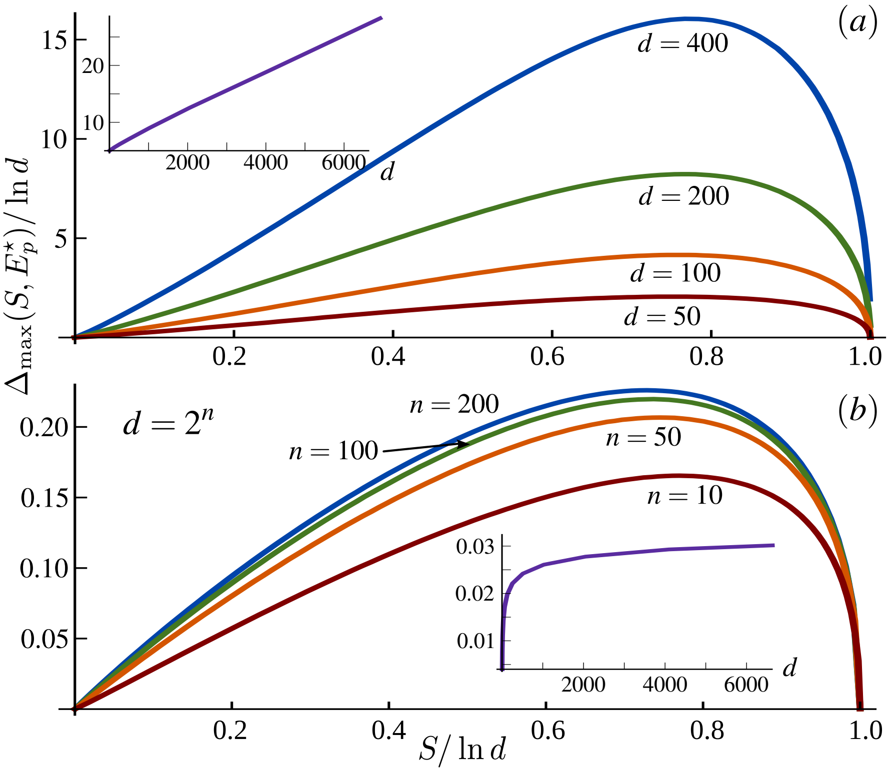

Figure 3.3.: $\Delta_{\max}(S, E_p^*)/\ln d$ versus $S/\ln d$ (a) for an equally spaced Hamiltonian with $d = 50, 100, 200, 400$; (b) for a collection of n non-interacting two level systems with $n = 10, 50, 100, 200$ (and $d = 2^n$). As the dimension increases, in (a) so does the energy difference between the most energetic passive state and the thermal state, while in (b) the difference grows much slower due to the presence of large degeneracies. Insets: $\Delta_{\max}(S, E_p^*)/\ln d$ versus d or n, for fixed small value of S. While in (a) there is linear growth, in (b) the value grows only logarithmically.

In this case, the number of states increases as $N_E \propto e^{nH(p)}$ where $p = E/n\epsilon$ can be interpreted as the local population. Figure 3.3 (case b) shows the computation of $\Delta_{\max}(S, E_p^*)$ as a function of S, and for different values of n- the dimension is given by $d = 2^n$. The figure shows that $\Delta_{\max}(S, E_p^*)$ grows sublinearly with n (i.e., slower than $\ln d$), and $\Delta_{\max}(S, E_p^*)$ remains very small even at very large energies/dimensions. This is in stark contrast with the case of an equally spaced Hamiltonian shown in the inset a) of the figure, where $\Delta_{\max}(S, E_p^*)$ grows linearly with d.

The example of Fig. 3.3 serves to illustrate that, for an exponential growth of the spectrum, not only both the energy and the entropy are extensive for the MEPS, but in fact the MEPS is very close to the thermal state itself. If true in general, this would have strong consequences. It would mean that, when dealing with Hamiltonians with an exponential DOS -those found, e.g., many-body systems locally interacting-, *all* passive states would behave pretty much in the same way, once either the energy or the entropy is fixed. This is in the spirit of the equivalence of canonical and microcanonical equilibria, that, again, holds only for systems with short range interactions (CDR09; BC15; MAMW15). It is worth adding that these type of spectra play an important role in fundamental questions such as thermalization (RGE12) or the third law (MO14).

3.3. The role of entanglement in work extraction

In this section we study a different aspect of activation processes, in particular the involved dynamics. The results presented are original and based upon (PLHH$^+$15b).

First of all, note that global unitary operations are necessary for activating passive states. Indeed, the state $\sigma_p^{\otimes n}$ can only be non-passive at the global level, as locally it is of course passive. Global operations are naturally related with the creation of entanglement, which makes one wonder what is the exact role played by entanglement in this process; and in particular whether there is a quantitative relation among the entanglement and the (global) extracted work.

Although a central motivation is to study work extraction from $\sigma_p^{\otimes n}$, our considerations apply to any initial diagonal state Ω in the energy basis,

$$\Omega = \sum_{\mathbf{i}} P_{\mathbf{i}} |\mathbf{i}\rangle\langle\mathbf{i}|, \tag{3.29}$$

so we keep the discussion general. As in Sec. 3.1, we have that $|\mathbf{i}\rangle = |i_1\rangle \cdots |i_n\rangle$ and the total Hamiltonian given by, $H^{(T)} = \sum_i h_i$, where $h_i = \sum_k \epsilon_k |k\rangle\langle k|$.

First note that diagonal states in the energy basis are not entangled. This follows because eigenstates of the Hamiltonian are separable (as the Hamiltonian is non-interacting), and hence any convex combination of them is also separable. Hence, even if one is using entangling operations, in an optimal work extraction process neither Ω nor the final state, which is passive and hence diagonal, are entangled. If entanglement appears, it does during the dynamical process. In this respect, in the next sections we address the following questions: does the state of the system get entangled during the process? If yes, how entangled does it become? Is there any way to bypass the entanglement creation, so that the state remains classically correlated all the time?

In the next sections we answer affirmatively the last question and provide a protocol that attains maximal work extraction with no entanglement generation at any time. The corresponding protocol is slow, in the sense that many operations are required. Then we consider faster protocols and provide lower bounds to the entanglement they generate.

3.3.1. Bypassing entanglement. Indirect paths.

To extract maximal work from a diagonal state we need to reorder its entries accordingly. This reordering can be done in elementary steps of transpositions. E.g., Ω may be such that the population of the lowest energy level (P_1) is not its maximal element, namely $P_{\nu\neq 1}$. Then one needs to transpose P_1 with P_ν, etc. After some number of such steps the state will be ordered properly, becoming passive.

The transposition of the population of any energy level by the population of some other level can be done without creating entanglement in the meantime. Indeed, suppose we need to transpose $P_{\mathbf{i}}$ by $P_{\mathbf{j}}$. The eigenstates of $H^{(T)}$ corresponding to them are $|\mathbf{i}\rangle = |i_1\rangle \cdots |i_n\rangle$ and $|\mathbf{j}\rangle = |j_1\rangle \cdots |j_n\rangle$, respectively. We then divide this action in $2n-1$ transposition steps. First

$$|i_1 i_2 ... i_n\rangle \rightleftarrows |j_1 i_2 ... i_n\rangle \rightleftarrows |j_1 j_2 ... i_n\rangle ... \rightleftarrows |j_1 j_2 ... j_n\rangle \tag{3.30}$$

and the $n-1$ steps back from $|j_1 j_2 ... j_{n-1} i_n\rangle$ to $|\mathbf{i}\rangle$. On each step one only exchanges the populations between states involved in it. Here we stress that all steps in (3.30) involve only the corresponding states, while the populations of the other states are kept unchanged. Thus, one cannot perform any of these steps with a local unitary operation.

The unitary operator that transposes the populations of two basis states, say

$|\mathbf{i}\rangle$ and $|\mathbf{j}\rangle$, reads as

$$U^{\mathbf{ij}} = \sum_{\mathbf{k}\neq\mathbf{i},\mathbf{j}} |\mathbf{k}\rangle\langle\mathbf{k}| + |\mathbf{i}\rangle\langle\mathbf{j}| + |\mathbf{j}\rangle\langle\mathbf{i}|. \tag{3.31}$$

If the control potential $V(t)$ generating $U^{\mathbf{ij}}$ couples only to $|\mathbf{i}\rangle$ and $|\mathbf{j}\rangle$, the evolution operator at some intermediate moment t of the process is

$$U^{\mathbf{ij}}(t) = \sum_{\mathbf{k}\neq\mathbf{i},\mathbf{j}} |\mathbf{k}\rangle\langle\mathbf{k}| + u^{\mathbf{ij}}(t), \tag{3.32}$$

where $u^{\mathbf{ij}}(t)$ lives in the linear span of $|\mathbf{i}\rangle$ and $|\mathbf{j}\rangle$ and is unitary. It depends on t and the concrete form of $V(t)$.

Now for, e.g., the first step in (3.30) we need to perform the transposition unitary $U^{\mathbf{ii}'}$ between $|\mathbf{i}\rangle = |i_1 i_2 ... i_n\rangle$ and $|\mathbf{i}'\rangle = |j_1 i_2 ... i_n\rangle$. According to (3.32) the global state of the system at an intermediate moment t is

$$\begin{aligned}\Omega(t) &= U^{\mathbf{ii}'}(t)\,\Omega\,U^{\mathbf{ii}'\dagger}(t)\\ &= (P_{\mathbf{i}} + P_{\mathbf{i}'})\,\rho_1(t) \otimes |i_2...i_n\rangle\langle i_2...i_n| + \sum_{\mathbf{k}\neq\mathbf{i},\mathbf{i}'} P_{\mathbf{k}} |\mathbf{k}\rangle\langle\mathbf{k}|.\end{aligned} \tag{3.33}$$

Quite straightforwardly, $\rho_1(t) \geq 0$ and $\mathrm{Tr}[\rho_1(t)] = 1$, so (3.33) means that the state is separable during the whole process of population exchange between $|\mathbf{i}\rangle$ and $|\mathbf{i}'\rangle$. Notice that although $U^{\mathbf{ii}'}(t)$ is global and thus has entangling power, there exist states which it does not entangle. By the same reasoning, one may stay separable also during the rest of transpositions in chain (3.30). So any replacement in the global state can be made without creating entanglement between its constituents, which proves that one can extract maximal work and stay separable during the whole process.

The previous non-entangling protocol requires $2n-1$ global operations in order to perform the desired exchange of the populations $|\mathbf{i}\rangle$ and $|\mathbf{j}\rangle$. However, this exchange can be performed in one step by the unitary operator (3.31). We term such evolutions by direct paths. Now, the natural question is whether entanglement is generated by these direct paths, which allow one to extract work faster and thus get more power.

3.3.2. Direct Paths

Consider the population exchange of $|\mathbf{i}\rangle$ and $|\mathbf{j}\rangle$. A relevant example of a direct path would be the time independent hamiltonian $H = \frac{\pi\hbar}{2\tau}\left(|\mathbf{i}\rangle\langle\mathbf{j}| + |\mathbf{j}\rangle\langle\mathbf{i}|\right)$ which generates the desired interchange at $t = \tau$. More generally, we will consider the evolution of $\Omega(t) = U^{\mathbf{ij}}\Omega U^{\mathbf{ij}\dagger}$ where $U^{\mathbf{ij}}$ is found from (3.32).

In order to measure the entanglement of $\Omega(t)$ in a direct path we use a recently proposed measure of genuine multipartite entanglement for mixed states (MCC$^+$11; HdV13; HPLdV13) which luckily turns out computable for states relevant to the work extraction protocol. The measure is essentially a generalisation of the concurrence to multipartite systems (see Appendix A.1 for a detailed description of the measure). The measure represents an ordered string E (with elements $E_1 \geq \cdots \geq E_{2^{n-1}-1} \geq 0$) called entropy vector (HdV13), which quantifies multipartite quantum correlations the following way: if the last $2^{l-1}-1$ entries of E are zero, then the state is l-separable (HPLdV13). In particular, (i) if $E_1 > 0$, then the state is entangled, and (ii) if $E_{2^{n-1}-1} > 0$ the state is genuinely multipartite entangled (GME).

In Appendix A.1 we bring closed-form expressions of lower bounds for all entries of the entropy vector. The states we deal with here have only two (complex-conjugated) nondiagonal elements (3.29, 3.32), which greatly simplifies the formulas. Their maximal values (reached simultaneously) during the transposition between $|\mathbf{i}\rangle$ and $|\mathbf{j}\rangle$, Λ_k, are given by (see Appendix A.1):

$$E_k \geq \Lambda_k = |P_{\mathbf{i}} - P_{\mathbf{j}}| - 2 \min_{A} \sum_{a \in \Gamma_A^k} \sqrt{P_{\mathbf{i}_a} P_{\mathbf{j}_a}}, \tag{3.34}$$

where a runs over all bipartitions $\gamma_a \cup \bar{\gamma}_a$ of the set $\{1, ..., n\}$; A enumerates the set of all k-tuples Γ_A^k of the index a; $|\mathbf{i}_a\rangle$ is obtained from $|\mathbf{i}\rangle$ by replacing i_k by j_k for all $k \in \gamma_a$; and analogously for $|\mathbf{j}_a\rangle$.

3.3.3. Entanglement generation in direct paths

Let us now explore expression (3.34) in more detail by focusing in the initial state being a product of passive states,

$$\Omega_p = \sigma_p^{\otimes n}. \tag{3.35}$$

with $\sigma_p = \text{diag}(p_1, ..., p_d)$. In the limit $n \to \infty$, the extractable work from $\sigma_p^{\otimes n}$ was shown in Sec. 3.1 to be,

$$\frac{W}{n} \overset{n\to\infty}{\longrightarrow} \text{Tr}\left[H(\sigma_p - \tau_{\beta'})\right] = \frac{1}{\beta'} S(\sigma_p || \tau_{\beta'}), \tag{3.36}$$

where $\tau_{\beta'} = \text{diag}(q_1, ..., q_d)$ is thermal and has the same entropy as σ_p, and $S(\,||\,)$ is the conditional entropy.

Let us now study the protocol described in Sec. 3.1, which allows to saturate the bound (3.35). Recall that the protocol consisted in exchanging the populations of the typical states of $\sigma_p^{\otimes n}$ with those of $\tau_{\beta'}^{\otimes n}$. In order to exchange all typical states, one needs to implement $e^{nS(\sigma_p)}$ transpositions, which not overlap and can therefore be made successively.

Consider the direct path exchange of the populations of $|\mathbf{i}\rangle$ and $|\mathbf{j}\rangle$ given, respectively, by $P_{\mathbf{i}} = \prod_{j=1}^{n} p_{i_j}$ and $P_{\mathbf{j}} = \prod_{j=1}^{n} p_{j_j}$. Here the expressions (3.34) are simplified to

$$E_k \geq |P_{\mathbf{i}} - P_{\mathbf{j}}| - 2k\sqrt{P_{\mathbf{i}} P_{\mathbf{j}}}. \tag{3.37}$$

So, e.g. for $P_{\mathbf{i}} \geq P_{\mathbf{j}}$, the state will be at most l-separable when:

$$\frac{P_{\mathbf{i}}}{P_{\mathbf{j}}} \geq 1 + 2\gamma + 2\sqrt{\gamma + \gamma^2}, \qquad \gamma = 2^{N-1} - 2^l + 1. \tag{3.38}$$

Now, pick one state from the typical set of $\sigma_p^{\otimes n}$, say $\bigotimes_{k=1}^{d} |k\rangle^{\otimes np_k}$, and transpose its probability $\prod_{k=1}^{d} p_k^{np_k}$ with $\prod_{k=1}^{d} p_k^{nq_k}$ – the population of the corresponding state $\bigotimes_{k=1}^{d} |k\rangle^{\otimes q_k}$ from the typical set of $\tau_{\beta'}^{\otimes n}$. Then, after some manipulation, we find that formula (3.38) implies the following condition

$$S(\tau_{\beta'}||\sigma_p) \geq \frac{1}{N} \ln \left[1 + 2\gamma + 2\sqrt{\gamma + \gamma^2}\right] \tag{3.39}$$

that σ_p must satisfy to be at most l-separable during the process. Here γ is the same as in (3.38). It can be easily checked that (3.39) is the same for all typical states, so it holds for the whole work extraction process.

Condition (3.39) has a simple interpretation – the greater the difference between σ_p and $\tau_{\beta'}$, the more entanglement we need. In the $n \gg 1$ limit, the condition for entanglement to be present is $S(\tau_{\beta'}||\sigma_p) \geq \ln[3 + 2\sqrt{2}]/n$ so basically all states get entangled, while the condition for genuine n-partite entanglement to appear is $S(\tau_{\beta'}||\sigma_p) \geq \ln[2]$ which tells that this entanglement does not have to be n-partite.

On the other hand, the extracted work is governed by the difference of σ_p and σ_{th} (3.36)-note the strong similarity of the expression for extracted work (3.36) and that for the entanglement generated in direct paths (3.39). So the further $\tau_{\beta'}$ is from σ_p, the more entanglement is generated and more work is extracted. For direct paths, there is hence a clear connection between the entanglement generated and the extracted work. This situation is illustrated in Fig. 3.4 for four three-level systems.

3.3.4. Entanglement and Power

This exemplary case shows that entanglement is widely present during direct exchanges. Furthermore, the amount of entanglement is directly connected to

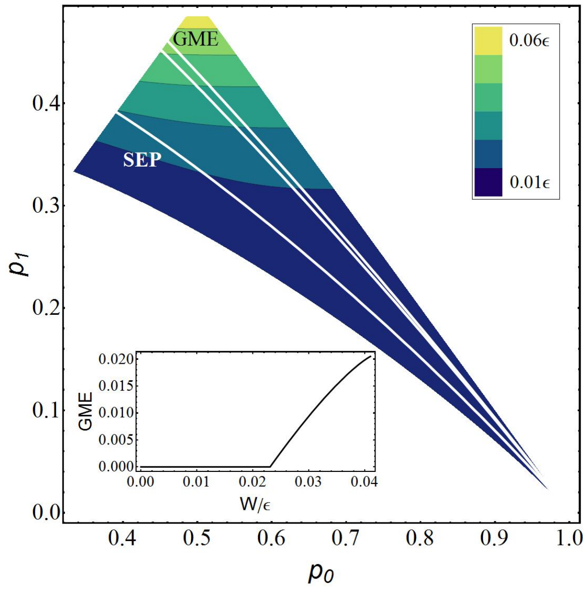

Figure 3.4.: A contour plot of the work W released by four three-level systems initially in the state $\otimes^4 \sigma_p$ on the direct path exchange of the populations of levels $|1111\rangle$ and $|0222\rangle$. The levels of each system are $\{0, \epsilon, \epsilon\}$. Lighter regions correspond to more work extraction. The white lines separate regions of l-separability, the left side (SEP) being fully separable and the rightmost region (GME) –genuinely multipartite entangled. The inset illustrates the direct quantitative relation between the amount of genuinely 4-partite entanglement measured by GME $= E_{2^{N-1}-1}$, and the extractable work W in the same setting and with $p_0 = 0.55$.

the amount of work for the case of identical systems. In general this connection exists but is less direct – work from an elementary exchange is proportional to the difference of populations involved, and so is the first term in (3.37) – the expression for generated entanglement.

On the other hand, the amount of generated entanglement can be reduced by combining direct and indirect paths. One simply performs $n-l$ exchanges via indirect paths followed by a direct path producing at most l-partite entanglement. Alternatively, (3.39) implies that for identical systems one can arbitrarily reduce the amount of entanglement generated by performing K extra steps of direct exchange of states ρ_k ($k = 1, ..., K$) satisfying $S(\rho_1||\sigma_p) < S(\rho_2||\sigma_p) < ... < S(\sigma_{\text{th}}||\sigma_p)$. In both cases, if we assume that all global transpositions are equally time consuming, reducing entanglement production comes at the expense of increasing the time of the process.

Our analysis thus suggests that, although entanglement plays no role for the amount of work one extracts, it may be crucial for the power – the larger the power output the more entanglement is created during the process. This strictly holds for the protocols considered here, and it does not depend on the choice of the entanglement measure. These considerations are in agreement with the theory of speed limits in quantum evolutions, where it has been shown that entangling operations allow to realize transformations faster than products of unitaries (GLM03). Finally, let us note that the converse problem, that of charging a set of quantum batteries, has been very recently studied in (BVMG15), and a clear relation between entanglement and the speed of the process has been observed.

3.4. Concluding remarks

In this chapter we have characterised the set of passive states, and also studied several aspects related to the phenomenon of activation.

In our first results, described in Sec. 3.2, we have found the family of passive states, the MEPS states, that maximise the energy of a system for a given entropy – and similarly minimise the energy for a given entropy. There is hence a clear parallelism with thermal states, which provide the reverse solution to such optimisations. These extremal properties allowed us to obtain a lower (upper) bound on the amount of extractable work from a single (collection of) passive(s) state(s). We have also discussed how energy and entropy are related for the MEPS depending on the spectrum of the Hamiltonian.

In the second project, we have studied the role of entanglement in activation processes, motivated by the observation that global (entangling) operations are necessary in this case. We have shown a relation between the entangled generated and the speed of the process- i.e., the more entanglement, the faster the process. These results are in agreement with considerations regarding speed limits (GLM03) and quantum batteries (BVMG15).

4. Work extraction from a quantum system in contact with a thermal bath

4.1. Introduction

Our considerations in the previous chapter singled out Gibbs states of the same temperature as completely passive states. Yet, when combined with other states, Gibbs states can become extremely useful for thermodynamic purposes, as they allow for transformations that are otherwise impossible. For example, two thermal baths at different temperature, each of them being of little use by itself, can be combined to create a heat engine. In fact, much of the theory of thermodynamics is concerned on the question of what are the possible operations when one combines a system with a thermal bath.

The joint evolution of system and bath is often studied under strong physical assumptions, such as weak coupling limit as well as specific system-bath interactions. Under such assumptions the evolution can be described through dissipative master equations (BP02). In the last years, new approaches to quantum thermodynamics, where generic evolutions between system and bath are allowed, have been put forward (see, e.g., (EVdB11; RW14; BaHO^{+}13; SSP14; WGE14)). In this chapter we take the framework of (EVdB11; RW14), and consider all unitary operations (or equivalently all cyclic processes) on system and an auxiliary Gibbs state at temperature β. Hence, note that what we call *bath* here is not a thermal bath in the standard sense of a macroscopic reservoir, but rather an auxiliary finite-dimensional Gibbs state.

Before moving forward, let us introduce some notation. Throughout this chapter we refer to the system as S and to the bath as B. ρ and γ correspond to the initial and final state respectively. For example, $\gamma_B = \mathrm{Tr}_S \gamma_{\mathrm{SB}}$ is the final state of the bath. We save the greek letter τ for Gibbs states at temperature β, e.g., $\tau_S = e^{-\beta H_S}/\mathcal{Z}_S$.

This Chapter is structured as follows. In Sec. 4.2, we present a derivation of the second law of thermodynamics -the derivation is original, although similar results were obtained before in (EVdB11; RW14). In Sec. 4.3, we present an explicit protocol saturating the second law which is inspired on the works of (SSP14; Abe13; AG13; RW14). In Sec. 4.5 and 4.5, we present our main original contributions, namely a derivation of restrictions to the second law arising from the finite size and the structure of the bath.

4.2. Second Law of Thermodynamics for Highly Controlled Operations

We start by discussing a generalization of the second law for arbitrary operations and initial states. Similar results to those presented in this section can be found in (EVdB11; RW14).

Consider a system S and an ancillary bath B with internal Hamiltonians H_{S} and H_{B}. Initially they are not interacting, and hence the total Hamiltonian is simply,

$$H = H_{\mathrm{S}} + H_{\mathrm{B}}. \tag{4.1}$$

We assume that initially S and B are also found in a product state,

$$\rho_{\mathrm{SB}} = \rho_{\mathrm{S}} \otimes \rho_{\mathrm{B}}, \tag{4.2}$$

where

$$\rho_{\mathrm{B}} = \tau_{\beta} = \frac{e^{-\beta H_{\mathrm{B}}}}{\mathcal{Z}}, \tag{4.3}$$

i.e., B is in a Gibbs state at inverse temperature β. No assumption is done on the initial state of S. We now consider general interactions between S and B (i.e., no weak coupling assumption) which can always be described by a unitary operation- we assume that the joint state of S+B remains thermally isolated. The final state after the interaction is hence given by,

$$\gamma_{\mathrm{SB}} = U \rho_{\mathrm{S}} \otimes \rho_{\mathrm{B}} U^{\dagger}. \tag{4.4}$$

In order to extend the definition of work here, and be able to apply our previous considerations to this setting, we treat SB as a "supersystem", which is thermally isolated, and hence the average extracted work is given by,

$$W = \mathrm{Tr}[H \rho_{\mathrm{SB}}] - \mathrm{Tr}[H \gamma_{\mathrm{SB}}], \tag{4.5}$$

where $H = H_{\mathrm{S}} + H_{\mathrm{B}}$. This quantity corresponds to the energy extracted by the external (time-dependent) sources. As suggested in Sec. 2.1.2, let us introduce the non-equilibrium free energy of S as,

$$F(\rho_{\mathrm{S}}) = \mathrm{Tr}(H_S \rho_{\mathrm{S}}) - T S(\rho_{\mathrm{S}}). \tag{4.6}$$

Now, adding and subtracting the difference of local entropies in (4.5), it can be rewritten as,

$$W = -\Delta E_{\mathrm{S}} - \Delta E_{\mathrm{B}} = -\Delta F_{\mathrm{S}} - \Delta F_{\mathrm{B}} - T(\Delta S_{\mathrm{S}} + \Delta S_{\mathrm{B}}) \tag{4.7}$$

Now we use the conservation of global entropy,

$$S(\gamma_{\mathrm{SB}}) = S(\rho_{\mathrm{SB}}) = S(\rho_{\mathrm{S}}) + S(\rho_{\mathrm{B}}). \tag{4.8}$$

and re express W as

$$W = -\Delta F_{\mathrm{S}} - \Delta F_{\mathrm{B}} - T I_{\mathrm{SB}} \tag{4.9}$$

where I_{SB} is the mutual information of the final state γ_{SB}. Now we use that, given any thermal state τ, the free energy difference to another (non-equilibrium) state ρ may be expressed through the relative entropy $S(\rho\|\tau) = -S(\rho) - \mathrm{Tr}(\rho \ln \tau)$ as $\Delta F = TS\left(\rho\|\tau(\beta)\right)$, obtaining that

$$W = -\Delta F_{\mathrm{S}} - T(S(\gamma_{\mathrm{B}}||\tau_{\mathrm{B}}) + I_{\mathrm{SB}}) \tag{4.10}$$

Equation (4.10), together with the related expession (4.12), are the main result of this section: They are exact relations, valid for any global unitary operation, between the extracted work from SB and the change of free energy of S. The main implication of (4.10) follows from the positivity of I_{SB} and $S(||)$, which leads to,

$$W \leq -\Delta F_{\mathrm{S}} \equiv F(\rho_{\mathrm{S}}) - F(\gamma_{\mathrm{S}}). \tag{4.11}$$

Remarkably, the latter expression only depends on the (initial and final) state of S and the temperature of B. We can drop the dependence on the final state of S by another straightforward manipulation,

$$W = -\Delta F_S^{\mathrm{th}} - T\left(S(\gamma_{\mathrm{S}}||\tau_{\mathrm{S}}) + I_{\mathrm{SB}} + S(\gamma_{\mathrm{B}}||\tau_{\mathrm{B}})\right), \tag{4.12}$$

where

$$\Delta F_S^{\mathrm{th}} \equiv F(\rho_{\mathrm{S}}) - F(\tau_{\mathrm{S}}) \tag{4.13}$$

and recall that, $\tau_{\mathrm{S}} = e^{-\beta H_S}/\mathcal{Z}_S$. Note that $-\Delta F_S \leq -\Delta F_S^{\mathrm{th}}$, and hence we can write the following chain of inequalities,

$$W \leq -\Delta F_S \leq -\Delta F_S^{\mathrm{th}} \tag{4.14}$$

where ΔF_S represents the change of free energies in a particular protocol (from ρ_{S} to γ_{S}); and ΔF_S^{th} is a bound on all possible work extraction protocols. The quantity ΔF_S^{th} is computed by the free energy difference between the initial state and taking as a final state the thermal state of S at the temperature of the bath. We will sometimes refer to ΔF_S^{th} as the *thermodynamic bound.* The power of the bounds (4.14) is that work, a magnitude which depends on the whole state of S and B as in (4.5), can be bounded by a function that depends only on the state of S and the temperature of B.

The strength of the bounds (4.14) is also their generality: They are derived assuming the possibility to implement any unitary operation on system and bath together. Furthermore, the equality form (4.12) allows to understand the origins of non-optimality in work extraction protocols. We can identify three:

1. the creation of correlations between system and bath, represented by the term I_{SB},
2. the bath being moved out from thermal equilibrium, represented by the term $S(\gamma_{\text{B}}||\tau_{\text{B}})$,
3. the system not reaching thermal equilibrium at the end of the process, quantified by $S(\rho_{\text{S}}^f||\tau_{\text{S}})$.

At a qualitative level, this allows us to understand why standard protocols in classical thermodynamics, where very little control is available, can surprisingly reach optimality: The interaction between system and bath is usually assumed to be weak, ensuring that I_{SB} remains small; and the bath remains in a thermal state throughout the protocol. In the next section we make this intuition precise by constructing a protocol that saturates the bound (4.12), which is inspired in a quasistatic evolution of the system.

4.3. Optimal Protocol

In this section we construct an explicit protocol, inspired on the works of (SSP14; Abe13; AG13; RW14), which is able to saturate (4.14). The protocol is well reminiscent of the classical works in thermodynamics, as it is based on a quasistatic evolution of ρ_S.

The protocol consists of n steps, which in the limit $n \to \infty$ and with a properly engineered auxiliary Gibbs state, extracts maximal work of ρ_S. Let us first construct the necessary auxiliary Gibbs state. It consists of a collection of n elements, each with Hamiltonian $H^{(i)}$ with the same dimension of H_{S}. The Hamiltonian of the first one is chosen such that,

$$\frac{e^{-\beta H^{(1)}}}{\mathcal{Z}_1} = \rho_S^{\text{passive}} \tag{4.15}$$

Note that this is always possible, as by appropriately constructing $H^{(1)}$ we can generate any passive state.[1] On the other hand, the Hamiltonian of the last bath element is chosen to satisfy,

$$H^{(n)} = H_S. \tag{4.16}$$

The other Hamiltonians are a linear interpolation between those two, i.e.,

$$H^{(i)} = \frac{i-1}{n} H_{\mathrm{S}} + \frac{(n-(i-1))}{n} H^{(1)}, \qquad i \in \{1, ..., n\}. \tag{4.17}$$

Note that it is satisfied

$$H^{(i+1)} = H^{(i)} + \frac{1}{n}(H^{(1)} - H_{\mathrm{S}}) \equiv H^{(i)} + x\Delta H \tag{4.18}$$

where $x = 1/n$. The total state of the bath is then simply given by,

$$\rho_{\mathrm{B}} = \bigotimes_i \rho_{\mathrm{B}}^i = \bigotimes_i \frac{e^{-\beta H^{(i)}}}{\mathcal{Z}_i}. \tag{4.19}$$

The protocol, i.e. the specific unitary operation U_{SB}, can be divided in two steps. In the first one, we bring ρ_{S} to a passive form,

$$\rho_{\mathrm{S}} \xrightarrow{U_{\mathrm{S}}} \rho_{\mathrm{S}}^{\text{passive}}. \tag{4.20}$$

where we notice that we act on S only. In the second step, we perform a collection of swaps between S and each element of the bath. In this process, the unitary operation U_{SB} can be decomposed as $U = \bigotimes_{i=1}^n U_i$ with,

$$U_i \rho_{\mathrm{S}} \otimes \rho_{\mathrm{B}}^i U_i^\dagger = \rho_{\mathrm{B}}^i \otimes \rho_{\mathrm{S}}. \tag{4.21}$$

The work extracted in the first step (4.20) is simply,

$$W_I = \mathrm{Tr}\left(H_{\mathrm{S}}(\rho_{\mathrm{S}} - \rho_{\mathrm{S}}^{\text{passive}})\right) = F(\rho_{\mathrm{S}}) - F(\rho_{\mathrm{S}}^{\text{passive}}), \tag{4.22}$$

where we used that the entropy of ρ_{S} and $\rho_{\mathrm{S}}^{\text{passive}}$ is the same. Let us now consider the second step, and divide the total work W_{II} into the sum of the work extracted after each swap, $W_{II} = \sum_i W_i$. The work extracted during particular swap U_j, using equality (4.10), can be expressed as,

$$W_i = F(\rho_{\mathrm{S}}^{j-1}) - F(\rho_{\mathrm{S}}^j) - S(e^{-\beta H^{(j)}}/\mathcal{Z}_j || e^{-\beta H^{(j-1)}}/\mathcal{Z}_{j-1}) \tag{4.23}$$

---

[1] The fact that, for a given H, not every passive state is Gibbs does not imply that by appropriately choosing H we can not generate any passive distribution.

where we used that $I_{\mathrm{SB}} = 0$ in a swap operation. Now we expand the second term of (4.23) in powers of $x \equiv 1/n$ using (4.18)

$$\begin{aligned} S(e^{-\beta H^{(j)}}/\mathcal{Z}_j || e^{-\beta H^{(j-1)}}/\mathcal{Z}_{j-1}) &= F(e^{-\beta H^{(j)}}/\mathcal{Z}_j) - F(e^{-\beta H^{(j-1)}}/\mathcal{Z}_{j-1}) \\ &= \frac{dF}{dx}\Big|_{x=0} x + \frac{1}{2}\frac{d^2F}{dx^2}\Big|_{x=0} x^2 + \mathcal{O}(x^3) \\ &= \frac{1}{2}\frac{d^2F}{dx^2}\Big|_{x=0} x^2 + \mathcal{O}(x^3) \end{aligned} \tag{4.24}$$

where we used that $dF/dx|_{x=0} = 0$ because the Gibbs state minimizes the free energy function. Therefore, adding up all the steps, we obtain,

$$W_{II} = F(\rho_S^{\text{passive}}) - F(\tau_S) - \sum_{i=1}^{n} \mathcal{O}(1/n^2) \tag{4.25}$$

The error term scales as $\mathcal{O}(1/n)$, and hence, in the limit $n \to \infty$, it tends to zero. Adding up the contribution of both protocols we finally obtain,

$$W = W_I + W_{II} = F(\rho_S) - F(\tau_S) + \mathcal{O}(1/n), \tag{4.26}$$

as desired.

Two important requirements are necessary to successfully implement this protocol:

1. the bath needs to be arbitrarily large, i.e., $n \to \infty$,
2. the auxiliary Gibbs states are engineered, in the sense that each Hamiltonian in (4.17) is carefully chosen and depends on ρ_S. Alternatively, one can assume the ability to prepare Gibbs states of any Hamiltonian.

In the next section we challenge both requirements, and study the limitations that finite-size and lack of engineering can impose on optimal protocols.

4.4. Finite Size Effects

In this section we use the exact equalities derived in Sec. 4.2 to obtain finite-size corrections to the principle of maximal work extraction. The results presented in this section are original and complement the work of (RW14), where finite-size corrections to the Landauer Principle where obtained. Note that, while both the Landauer principle and the maximal work extraction principle can be seen as formulations of the second law, the finite-size corrections depend on the specific formulation. For example, unlike in Ref. (RW14), our considerations depend explicitly on the Hamiltonian of S.

Here we assume that S has a hamiltonian H_{S} with dimension d_{S}, whereas the Hamiltonian of B is free, and only its dimension d_B is fixed. Let us rewrite (4.12) as

$$W = -\Delta F_S^{\mathrm{th}} - TS(\gamma_{\mathrm{SB}}||\tau_{\mathrm{SB}}). \tag{4.27}$$

The point is to minimise $S(\gamma_{\mathrm{SB}}||\tau_{\mathrm{SB}})$ over all H_{B} and γ_{SB}, for a fixed dimension d_{B}. For any H_{B}, $S(\gamma_{\mathrm{SB}}||\tau_{\mathrm{SB}}) = F(\gamma_{\mathrm{SB}}) - F(\tau_{\mathrm{SB}})$ is always minimized when γ_{SB} is a Gibbs state, as they minimise the free energy function. Its temperature is determined by the condition $S(\rho_{\mathrm{SB}}) = S(\gamma_{\mathrm{SB}})$. Let then τ'_{SB} be a Gibbs state which satisfies $S(\rho_{\mathrm{SB}}) = S(\tau'_{\mathrm{SB}})$, we then obtain,

$$S(\gamma_{\mathrm{SB}}||\tau_{\mathrm{SB}}) \geq S(\tau'_{\mathrm{SB}}||\tau_{\mathrm{SB}}) = S(\tau'_{\mathrm{S}}||\tau_{\mathrm{S}}) + S(\tau'_{\mathrm{B}}||\tau_{\mathrm{B}}) \geq S(\tau'_{\mathrm{B}}||\tau_{\mathrm{B}}). \tag{4.28}$$

We can now minimise $S(\tau'_{\mathrm{B}}||\tau_{\mathrm{B}})$ over all Hamiltonians H_{B}. In (RW14), it is proven that this minimisation is obtained when H_{B} takes the form,

$$H_{\mathrm{B}}^* = \mathrm{diag}(0, \epsilon, ..., \epsilon), \tag{4.29}$$

i..e, a Hamiltonian with only two levels, the highest one having a degeneracy of $d_{\mathrm{B}} - 1$. The value of ϵ can be determined by a numerical optimisation. More concretely, expressing $S(\tau'_{\mathrm{B}}||\tau_{\mathrm{B}})$ for H_{B}^*, we obtain,

$$S(e^{-\beta' H_{\mathrm{B}}^*}/\mathcal{Z}'||e^{-\beta H_{\mathrm{B}}^*}/\mathcal{Z}) = \frac{\ln(1 + (d_{\mathrm{B}} - 1)e^{-\beta\epsilon})}{\beta} - \frac{\ln(1 + (d_{\mathrm{B}} - 1)e^{-\beta'\epsilon})}{\beta'} \equiv \kappa(\beta', \epsilon). \tag{4.30}$$

On the other hand, the condition $S(\tau'_{\mathrm{SB}}) = S(\rho_{\mathrm{SB}})$, which determines β', can be now expressed as,

$$S\left(\frac{e^{-\beta'(H_{\mathrm{S}} + H_{\mathrm{B}}^*)}}{\mathcal{Z}'_{\mathrm{SB}}}\right) = S(\rho_{\mathrm{S}}) + S\left(\frac{e^{-\beta H_{\mathrm{B}}^*}}{\mathcal{Z}_{\mathrm{B}}}\right). \tag{4.31}$$

Putting everything together, we obtained that,

$$S(\gamma_{\mathrm{SB}}||\tau_{\mathrm{SB}}) \geq \min_{\epsilon}\left(\kappa(\beta', \epsilon)\right) \tag{4.32}$$

subject to the constraint (4.31). This minimisation can be carried out numerically in a straightforward way (as it involves only two real parameters). Importantly, the result only depends on β and d_{B}, and hence it can be interpreted as a finite-size correction to the second law, $W \leq -\Delta F^{\mathrm{th}}$.

Observe that, as $d_\mathrm{B}/d_\mathrm{S} \gg 1$, the corrections tend to zero. In this case, in the expression that determines β', given by (4.31), the entropy of S becomes negligible with respect to the entropy of B, which leads to $\beta' \to \beta$. In such a case, the right hand side of (4.32) tends to zero.

Finally, it is important to stress that the fact that the Hamiltonian H_B^* can be used to minimise the relative distance between states does not mean that H_B^* is a good Hamiltonian for a work extraction protocol. The presence of only one gap in H_B^* makes it impossible to achieve slow quasi static transformation of the system, in the spirit of the protocol described in Sec. 4.3, which makes it a bad candidate for work extraction. Hence, while formally tight, we do not expect our bounds to be reachable when considering specific work extraction protocols.

4.5. Restricted Bath

In this section we study how the structure of the bath limits the possibility of achieving the thermodynamic bound, and in particular we present some original results about the limitations that appear when one uses a system made up of n-level systems as a thermal bath for work extraction.

A crucial property of the optimal protocol described in Sec. 4.3 is the possibility to prepare Gibbs state of any Hamiltonian. While this can be motivated by the fact that thermal baths are expected to thermalise any system that is put in weak contact with them, when dealing with highly controllable operations it is conceivable to imagine that we have only access to a particular set of states. In this section we illustrate the consequences of this limitation by considering a bath made up of the simplest quantum system, namely n 2-level systems, or qubits, with *identical* gap δ. That is, our free resource is restricted to bath of qubits with a fixed gap δ. In this case, the initial state reads,

$$\rho_\mathrm{SB} = \rho_S \otimes \tau_\beta^{\otimes n}. \tag{4.33}$$

where $\rho_S = \mathrm{diag}\{1-p, p\}$ and $\tau_\beta = \mathrm{diag}\{1-q, q\}$. Note that, without loss of generality, we assume that S starts in a passive state, as it can be brought into this form with a local unitary acting on S only. Since SB together are thermally isolated, the maximal amount of work from ρ_SB reads,

$$W_\mathrm{max} = \mathrm{Tr}\left((H_\mathrm{S} + H_\mathrm{B})(\rho_\mathrm{SB} - \rho_\mathrm{SB}^\mathrm{passive})\right) \tag{4.34}$$

where we note that, unlike in free energy like bounds, this expression depends on the specific state of the bath. Our aim is then compare W_max with the thermodynamic bound given by the difference of free energies, ΔF^th.

In order to be able to extract work from SB, ρ_{SB} must be a non-passive state. Since ρ_{SB} is diagonal, non-passivity is equivalent to the presence of population inversions. There is a population inversion between two states A and B if $E_{\mathrm{A}} < E_{\mathrm{B}}$ and $p_{\mathrm{A}} > p_{\mathrm{B}}$, or vice versa. Taking $E_A = k\delta$, $p_A = (1-p)q^k(1-q)^{n-k}$ and $E_{\mathrm{B}} = k'\delta + \epsilon$, $p_B = pq^{k'}(1-q)^{n-k'}$, we can easily derive a condition for the appearance of population inversions,

$$\min\left\{\frac{\beta_{\mathrm{S}}}{\beta}, 1\right\} \leq x\frac{\delta}{\epsilon} \leq \max\left\{\frac{\beta_{\mathrm{S}}}{\beta}, 1\right\}, \qquad x = 1, 2, 3, ..., n \tag{4.35}$$

where $x = |k - k'|$, and $\beta_{\mathrm{S}} = \ln(\frac{1-p}{p})$, $\beta = \ln(\frac{1-q}{q})$ are the temperature of S and B respectively. Whenever (4.35) is not satisfied, then $W_{\max} = 0$ and no work can be extracted in any protocol. Note that this $W_{\max} = 0$ is perfectly compatible with $\Delta F^{\mathrm{th}} \neq 0$, which holds as long as $\beta \neq \beta_{\mathrm{S}}$. The fact that $W_{\max} \ll \Delta F^{\mathrm{th}}$ just means that the auxiliary Gibbs state $\tau_\beta^{\otimes n}$ is particularly bad for work extraction purposes.

Without the need of computing explicitly $W_{\max}$, we can qualitatively understand some of its properties from condition (4.35). In particular, if $\delta > \epsilon$ and $\beta\delta > \beta_{\mathrm{S}}\epsilon$, the condition cannot be satisfied, and hence $W_{\max} = 0$. Therefore we expect regimes where either $\delta \gg \epsilon$ (i.e., the energy scale of S is smaller than that of the components of the bath) or $\beta \gg \beta_{\mathrm{S}}$ (i.e., low temperatures) is satisfied to not allow for work extraction. Note that in such regimes quantum effects are particularly relevant. On the other hand, the fact that x in (4.35) takes natural numbers, suggests that the regions where work extraction is possible can be disconnected.

These considerations are illustrated in Figs. 4.1 and 4.2, where we have computed $W_{\max}$ as a function of δ in two different scenarios. It is important to note that the computations were done for baths of a remarkable size, e.g., in the figures we took 500 qubits. This was only possible because of the high amount of degeneracies present in the initial state of the bath, which allows us to describe it with $\mathcal{O}(n)$ parameters. For such big baths, we observe in Fig. that $W_{\max}$ becomes zero for $\delta > \epsilon$, as it can be anticipated from condition (4.35). Conditions (4.35) also characterise the regions where work extraction is possible, as each value of x in (4.35) yields a possible set of δ where the state becomes non-passive. On the other hand, the figures also show how the different free energies defined in (4.14) come into play. The thermodynamic bound, given by $W \leq -\Delta F^{\mathrm{th}}$, is constant as it only depends on ρ_{S}; whereas the change of free energies ΔF depends on both the initial and final state of the work extraction protocol and hence it yields a better estimation of $W_{\max}$.

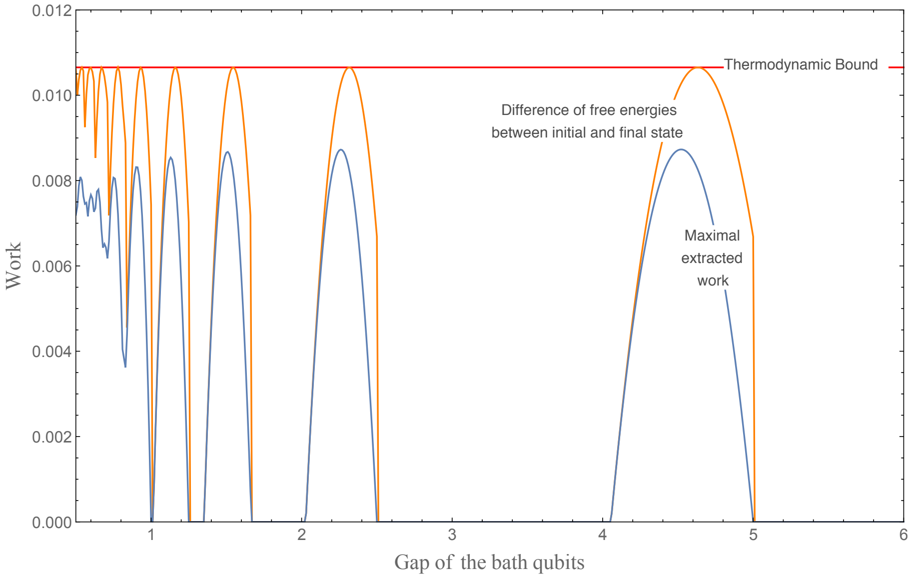

Figure 4.1.: Maximal extractable work (in blue), free energy difference (in orange) and the thermodynamic bound (in red) as a function of δ. The maximal extractable work $W_{\max}$ (which is computed through 4.34). We take for $\epsilon = 5$, $\beta = 0.3$, and $p = 0.4$. Observe that $W_{\max}$ never reaches the thermodynamic bound.

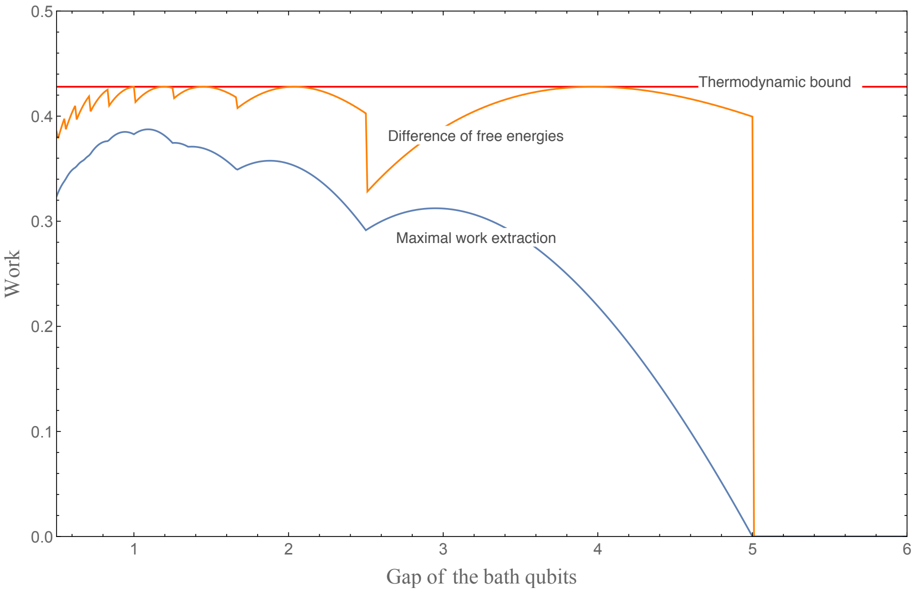

Figure 4.2.: Maximal extractable work (in blue), free energy difference (in orange) and the thermodynamic bound (in red) as a function of δ. The maximal extractable work $W_{\max}$ (which is computed through 4.34). We take for $\epsilon = 5$, $\beta = 0.3$, and $p = 0.4$.

4.6. Activation

In this section we present some original results which show how the limitations presented in the last section can disappear if one takes systems of increasing size.

The previous section suggests that fine-tuning of the bath is necessary in order to achieve optimality in work extraction protocols. In particular, for a bath made up of n qubits, we showed that even in the macroscopic limit, no work can be extracted from S even though the free energy of the state would have suggested otherwise. In this section we show that, using the very same bath, this limitation can be overcome and hence obtain $W \to \Delta F_{\mathrm{th}}$ if one considers several copies of S, i.e., we take as an initial state $\rho_0 = \rho_{\mathrm{S}}^{\otimes k} \otimes \rho_{\mathrm{B}}^{\otimes n}$. This result is in the same spirit of the activation of passive states presented in Sec. 3.1. We now prove that $W_{\max} \to \Delta F_{\mathrm{th}}$ for any δ in the limit $n, k \to \infty$ with $k^2/n \to 0$, by adapting the main result of (BaHO+13).

Let us assume there there exists a U which performs the following transformation,

$$\rho_{\mathrm{S}}^{\otimes k} \otimes \tau_{\mathrm{B}}^{\otimes n} \to \tau_{\mathrm{S}}^{\otimes k} \otimes \gamma_{\mathrm{B}}^{\otimes n}, \tag{4.36}$$

The associated energy change is $W = k\epsilon\Delta p + n\delta\Delta q$, which is bounded by $\Delta F_{\mathrm{th}} = k\epsilon\Delta p - kT(S(\rho_{\mathrm{S}}) - S(\tau_{\mathrm{S}}))$. By using the conservation of entropy, $kS(\rho_{\mathrm{S}}) + nS(\tau_{\mathrm{B}}) = kS(\tau_{\mathrm{S}}) + nS(\gamma_{\mathrm{B}})$, we can relate W with ΔF^{th}, obtaining

$$\Delta F_{\mathrm{th}} - W = Tn\left(S(\tau_{\mathrm{B}}) - S(\gamma_{\mathrm{B}}) - \beta\delta\Delta q\right) = \frac{1}{2q_{\mathrm{th}}(1-q_{\mathrm{th}})} n\Delta q^2 + \mathcal{O}\left(\frac{n}{k}\Delta q^3\right), \tag{4.37}$$

where we Taylor expanded for $\Delta q \to 0$. To justify such an expansion, note that in any positive work extracting process $0 \leq W \leq \Delta F_{\mathrm{th}}$, it is satisfied

$$-\frac{k}{n}\frac{\epsilon\Delta p}{\delta} \leq \Delta q \leq \frac{k}{n} T(S(\rho_{\mathrm{S}}) - S(\rho_{\mathrm{f}})) \tag{4.38}$$

which implies that Δq scales as k/n. Plugging this dependence into (4.37) we obtain,

$$W = \Delta F^{\mathrm{th}} - \mathcal{O}(k^2/n). \tag{4.39}$$

which shows that, in the limit $k^2/n \to 0$ it is in principle possible to find a protocol (i.e., a unitary operation) that reaches optimality. Let us stress that this result is independent of δ, and therefore no engineering of the bath is necessary.

Let us now construct explicitly the unitary implementing (4.36) by using notions of typicality, as in Sec. 3.1, or see also Refs. (AF13; BaHO+13). In the limit $k, n \to \infty$, ρ_0 is well described by a mixture of $2^{kS(\rho_{\rm S})+nS(\rho_{\rm S})}$ *typical states*, i.e., basis states with energy $nq\delta + kp\epsilon + \pm\mathcal{O}(\sqrt{N}, \sqrt{k})$. The error in such a description is exponentially small with both k and n. On the other hand, the final state can be described by the same number of typical states since it has the same entropy as ρ_0. Therefore, we can construct a U which maps the typical states of the initial state to those of the final state, and thus it effectively implements (4.36). In order to ensure that (4.39) holds while $k \to \infty$, one can take $k \propto n^{1/4}$. Alternatively, if one only desires to obtain optimality for each copy, i.e., $(\Delta F^{\rm th} - W)/k \to 0$, taking $k \propto n^{1/2}$ suffices.

In Sec. 4.2 we identified three properties of optimal protocols for work extraction: no correlations are created between system and bath, and both S and B are in thermal equilibrium at the end of the process. It is easy to see that the protocol constructed here satisfies the three of them. Indeed, the final state in (4.36) is a product state, and thus $I_{\rm SB} = 0$. The system has reached thermality, so that $S(\gamma_{\rm S}||\tau_{\rm S}) = 0$. Finally, even if the state of B is not completely thermal at the end, it follows from (4.38) that each bath qubit is only perturbed an amount $\Delta q \sim 1/n$ in the limit of large n. Then, one easily obtains $nS(\gamma_{\rm B}||\tau_{\rm B}) \sim 1/n$ by expanding $S(||)$ around $\Delta q \to 0$.

Finally, we can extend the condition for the appearance of population inversions, given in 4.35, for the case where k copies of S are available, obtaining,

$$\min\left\{\frac{\beta_{\rm S}}{\beta}, 1\right\} \leq x\frac{\delta}{\epsilon} \leq \max\left\{\frac{\beta_{\rm S}}{\beta}, 1\right\}, \qquad x = \frac{a}{b}, \tag{4.40}$$

where $a = \{1, 2, ..., n\}$ and $b = \{1, 2, ..., k\}$. Thus, if k and n are big, then population inversions appear for most δ. This can be understood as another form of activation, when copies of a passive state are considered in the presence of an auxiliary Gibbs state.

4.7. Connections to other frameworks: From time dependent fields to fully energy preserving operations.

In this section we present some connections between the framework used in this Chapter for studying work extraction processes and other approaches to deal with work extraction in quantum systems, in particular the resource theory of thermodynamics (BaHO$^+$13), which provides a fully quantum treatment to thermodynamics.

Up to this point, we have considered S and B to be a thermally isolated system. In this case, the energy is extracted from (or put into) SB by time dependent fields, which can generate unitary operations that do not commute with $H_{\mathrm{S}} + H_{\mathrm{B}}$. While dealing with time dependent fields is motivated from an experimental point of view (indeed, they are used to transform and deal with microscopic quantum systems), from a fundamental point of view it might be unsatisfactory to accept that work is extracted or input through semi-classical fields. For a complete quantum picture, one needs to treat explicitly the energy storage, which gives an extract energy from SB. This energy storer is often referred to as a weight W. The possibilities and implications of having an explicit energy storer in thermodynamic protocols has attracted a lot of interest in the last years, see Refs. (LPS10; BaHO^{+}13; Abe14; SSP14; FJR14; GA15; GEW15) for relevant works in this direction. It is the purpose of this section to describe how our considerations can be adapted to this framework.

4.7.1. Framework

When dealing with an energy storer, or a battery, we shall assume a non-interacting Hamiltonian at the beginning of the process, of the form,

$$H_{\mathrm{SBW}} = H_{\mathrm{S}} + H_{\mathrm{B}} + H_{\mathrm{W}} \tag{4.41}$$

The Hamiltonian of the battery is assumed to be dense and non-degenerate, so that it can accept and give any amount of work,

$$H_{\mathrm{W}} = \int w|w\rangle\langle w| dw. \tag{4.42}$$

On the other hand, the initial state of the work extraction protocol takes the form

$$\rho_{SBW} = \rho_{\mathrm{S}} \otimes \tau_{\mathrm{B}} \otimes \rho_{\mathrm{W}}, \tag{4.43}$$

where unless said explicitly, no assumption is made on the state of the weight, ρ_{W}.

The main new ingredient within this framework is that, since the energy is provided and located in the battery, the full system is closed and hence the operations preserve the total energy. More precisely, strict energy conservation can be expressed as,

$$[H_{\mathrm{SBW}}, U_{\mathrm{SBW}}] = 0. \tag{4.44}$$

It follows from this condition that, for *any* ρ_{SBW}, we obtain,

$$\Delta E_{\mathrm{S}} + \Delta E_{\mathrm{B}} + \Delta E_{\mathrm{W}} = 0. \tag{4.45}$$

Following we will discuss possible definitions of work and formulations of the second law within these frameworks, to later build explicitly connections between this framework and the one used throughout the thesis.

4.7.2. Second laws of thermodynamics in the presence of a weight

From the conservation of the total average energy, we obtain,

$$\Delta E_{\mathrm{W}} = -\Delta E_{\mathrm{S}} - \Delta E_{\mathrm{B}}, \tag{4.46}$$

Adding and subtracting the local differences of entropies, and by doing a manipulation similar to (4.10), we obtain,

$$\Delta F_{\mathrm{W}} = -\Delta F_{\mathrm{S}} - T(S(\gamma_{\mathrm{B}}||\tau_{\mathrm{B}}) + I_{\mathrm{SBW}}), \tag{4.47}$$

where $I_{SBW} \equiv S(\gamma_S) + S(\gamma_B) + S(\gamma_W) - S(\gamma_{SBW})$ quantifies the correlations generated in the tripartite system. Since $I_{SBW} \geq 0$ and $S(\gamma_{\mathrm{B}}||\tau_{\mathrm{B}}) \geq 0$, we have that

$$\Delta F_{\mathrm{W}} \leq -\Delta F_{\mathrm{S}}. \tag{4.48}$$

If no assumptions are made on the state of the weight and the process U_{SBW}, this relation is probably the most natural generalisation of the second law, where work would be here identified with ΔF_{W}. This expression asserts that the amount of free energy that can be transferred from the energy to the weight is bounded by the free energy of the system itself. This naturally causes some *degradation* of the free energy. If, after the first process, we were to use the weight to raise a second weight (i.e., the first weight would become the system), the extracted work would generically be less (being only the same when optimality in both processes is reached). Identifying work as the change of free energy of the weight have been suggested independently in Ref. (GA15), following a similar reasoning that the one discussed here, and in Ref. (GEW15), where an axiomatic approach is advocated.

Another approach for dealing with work extraction with an explicit energy storage system is to associate work with the average change of energy of the weight, ΔE_{W}. This is motivated by the first works of Carnot in thermodynamics, where one quantifies useful work by the amount of energy that a weight is raised. In this case, the first trivial observation is that, from (4.48), it is obvious that ΔE_{W} can be larger than $-\Delta F_{\mathrm{S}}$ if one uses the weight as an entropy sink, i.e., $\Delta S_{\mathrm{W}} < 0$. In order to avoid this possibility, the authors of (SSP14) impose the following restrictions on the allowed protocols U_{SBW},

- *Weight-state independence*: in any allowed protocol ΔE_{W} must be independent of the initial state of the weight.

- *Weight-translation invariance*: any allowed U_{SBW} must commute with translation operations on the weight.

The first condition ensures that the weight can not be used as an entropy source, as $\Delta S_{\mathrm{W}} < 0$ can not be smaller than zero for every ρ_{W}. Using such two conditions, one can derive a second-law-like expression relating ΔE_{W} with ΔF_{S} (SSP14).

Finally, an important line of research in the framework of global energy-preserving operations is the study of single-shot work extraction (DRRV11; Abe13; HO13). Here one defines work as a deterministic change of energy in the weight. In this framework the weight- usually described by a qubit system- starts initially in a the ground state, and in a successful work extraction protocol it ends in the excited state. Note that here work is not a fluctuating variable, but a deterministic one, which is motivated by the fact that work is usually associated with ordered energy. For this definition of work, one cannot reach $W_{\mathrm{det}} \to \Delta F^{\mathrm{th}}$, but rather work is bounded by one-shot generalizations of the free energy (Abe13; HO13).

As a final remark, we would like to express the opinion of the present author on the matter of the definition of work. Here we have briefly presented three definitions of work, all of them leading to meaningful expressions of the second law (under appropriate conditions). We believe that this should not be seen as an inconsistency, because, in our opinion, the main point of quantum thermodynamics is to establish relations (that are as general as possible) for quantities that are operationally well defined. All the definitions here are examples of such operational quantities, and hence, independently of what we call what, it seems a priori equally relevant the study of them. This could change if, as it happens in macroscopic thermodynamics, there are direct applications which favour one definition of work over the other.

Explicit connections between the different frameworks

Let us now explicitly relate time-dependent operations U_{SB} with the time-independent U_{SBW} ones, i.e., unitaries that satisfy $[H_{\mathrm{S}} + H_{\mathrm{B}} + H_{\mathrm{W}}, U_{\mathrm{SBW}}] = 0$. We would like to find, for every work extraction protocol V_{SB} in SB, a corresponding work extraction protocol V_{SBW} in SBW that extracts the same amount of work. For simplicity we focus on the case where work is identified with the change of average energy on the weight ΔE_{w}. The problem is then to find a V_{SBW} for every V_{SB} such that,

$$\begin{aligned}&\mathrm{Tr}\left(H_{\mathrm{W}}\left(\mathrm{Tr}_{\mathrm{S,B}}\left(V_{\mathrm{SBW}}\rho_{\mathrm{S}} \otimes \tau_{\mathrm{B}} \otimes \rho_{\mathrm{W}} V_{\mathrm{SBW}}^{\dagger}\right) - \rho_{\mathrm{W}}\right)\right)\\ &\qquad = \mathrm{Tr}\left((H_{\mathrm{S}} + H_{\mathrm{B}})(V_{\mathrm{SB}}\rho_{\mathrm{S}} \otimes \tau_{\mathrm{B}} V_{\mathrm{SB}}^{\dagger} - \rho_{\mathrm{S}} \otimes \tau_{\mathrm{B}})\right) \qquad (4.49)\end{aligned}$$

where $[H_{\mathrm{S}} + H_{\mathrm{B}} + H_{\mathrm{W}}, V_{\mathrm{SBW}}] = 0$.

For clarity, let us write the Hamiltonian of SB as,

$$H_{\mathrm{SB}} = \sum_i E_i |i\rangle\langle i|, \tag{4.50}$$

where $|i\rangle = |\epsilon\rangle_{\mathrm{S}}^{(\mathrm{i})} \otimes |\delta\rangle_{\mathrm{B}}^{(i)}$ and $E_i = \epsilon_{\mathrm{S}}^{(i)} + \delta_{\mathrm{B}}^{(i)}$. Then we can write any unitary operation on SB as,

$$U_{\mathrm{SB}} = \sum_{ij} u_{ij} |i\rangle\langle j|. \tag{4.51}$$

Consider now the following energy preserving unitary on the extended space of SBW,

$$V_{\mathrm{SBW}} = \sum_{ij} u_{ij} |i, x - (E_i - E_j)\rangle\langle j, x|. \tag{4.52}$$

It is indeed easy to check that V_{SBW} commutes with the global Hamiltonian of SBW. For simplicity, let us know focus on states ρ_{S} that are diagonal in the basis of H_{S}. In this case, we have that,

$$\rho_{\mathrm{SB}} = \sum_i p_i |E_i\rangle\langle E_i|. \tag{4.53}$$

An straightforward computation then yields,

$$\mathrm{Tr}\left(H_{\mathrm{W}} \mathrm{Tr}_{S,B}\left(V_{\mathrm{SBW}} \rho_{\mathrm{SB}} \otimes \rho_{\mathrm{W}} V_{\mathrm{SBW}}^{\dagger}\right)\right) = \mathrm{Tr}\left(H_{\mathrm{W}} \rho_{\mathrm{W}}\right) - \sum_{i,j} p_i |u_{ji}|^2 (E_j - E_i) \tag{4.54}$$

From this expression it is simple to show that indeed V_{SBW} satisfies condition (4.49). This shows that, when dealing with diagonal states of the system, any protocol derived within the framework of time dependent fields can be translated to the framework of energy conserving operations by identifying work with the average energy that the battery gains. Importantly, this result holds independently of the state of the battery.

When dealing with coherent states, the situation is more subtle. It is easy to see that the computation (4.54) does not work when the state of S has coherences. In fact, dealing with coherences with strictly energy preserving operations is known to be a hard task, see for relevant references (SSP13; Abe14; LJR14; LKJR15; iaCanSanHO15). When it comes to the problem of work extraction, an important insight was given by in Ref (Abe14) (see also related work in Ref. (MSK15; KLOJ15)), where it was shown that if one chooses the state of the battery to be a fully coherent state,

$$\rho_{\mathrm{W}} = |\psi\rangle\langle\psi|, \quad |\psi\rangle = \frac{1}{L} \sum_{w=-L/2}^{L/2} |w\rangle \tag{4.55}$$

where $H_\mathrm{W} = \sum w|w\rangle\langle w|$, then in the limit $L \to \infty$, one successfully obtains (4.49) for this particular state of the weight. The intuition behind this result can be understood by first noting that the operation (4.52) induces shifts on the energy state of the weight. If the state of the weight is localized in a single eigenstate, then a back reaction will appear due to the correlations created when interacting with SB. However, in the case of a fully coherent state, the state becomes an eigenstate of the shift operator, and hence there is no back action at all.

Summarizing, in this section we have pointed out that the two frameworks presented in this thesis, time dependent fields and energy preserving unitaries, can be related through the transformation (4.52). In the case of diagonal states of S, then essentially any state of the battery works, but when dealing with coherences the correspondence holds only in the limit of a fully coherent state of the battery. More details on the connection between both frameworks can be found in Refs. (Abe14; MSK15; KLOJ15).

4.8. Concluding Remarks

In this chapter we have first derived the second law of thermodynamics in a very general setting, by considering arbitrary unitary operations on system and bath together (see (EVdB11; RW14) for similar results). This has been possible by obtaining an exact expression that relates the extracted work with the change of free energy of the state. From this relation it follows that work is bounded by the free energy difference, and at the same time it shows explicitly the origins of non-optimality. Those are the generation of correlations between system and bath, and lack of thermal equilibrium at the end of the process. In this sense, we note that neither quantum effects such as entanglement nor a high level of control can lead to any violation of the second law of thermodynamics: This law can be naturally extended to out of equilibrium processes in the quantum regime.

The bath has been represented by a completely passive state, i.e., a Gibbs state of a given temperature. Else, no assumption is made on it, neither on its structure nor on its size. Therefore, our considerations apply to standard thermal macroscopic reservoirs, but also to auxiliary Gibbs states made up of, e.g., a few quits. This big range of applicability has allowed us to study the implications of size and structure of the bath for work extraction in the quantum regime. In the first place, we have derived finite-size limitations to the principle of maximal work extraction, which only depend on the dimensionality of the bath and its temperature. Secondly, we have considered baths made up of identical two-level systems. For such a specific structure, we have encountered strong limitations on the work we can extract when either the temperature of the bath is very low or the size of the energy gap of the bath is bigger than that of the system. Indeed, in such regimes, even if we assume that any unitary can be performed on system and bath, none of the free energy of the state can be extracted. This illustrates the difficulty of extracting work from microscopic quantum systems. To further strengthen this observation, we have also shown that, as the size of the system increases (which we have illustrated by taking copies of it), work extraction becomes possible and it progressively tends to the free energy bound. Hence, we recover the standard results in the macroscopic limit; while showing that strong limitations can show up when dealing with small quantum systems.

Finally, we have discussed how the framework considered here, unitary evolutions on system and bath, can be extended to the fully quantum case, where energy is extracted and put into the system by an explicit energy storer, a battery.

5. Quantum Fluctuations of Work

5.1. Introduction

Understanding fluctuations of thermodynamic work has always been of central interest to statistical thermodynamics. Not only they provide an exhaustive description of the work variable, but also, through Jarzynski-Crooks relations, they serve as a bridge between equilibrium and nonequilibrum thermodynamics (see (SPWS08; EHM09; CHT11) for reviews on the topic). In the quantum realm, however, the very definition of work is a matter of debate, and hence it is not surprising that characterising its fluctuations is a difficult task. This difficulty has two basic origins: The first one is that work is associated with a process, rather than an instantaneous state of the system, and hence it cannot be described by a standard Hermitian operator. The second one is that measurements in quantum physics generically disturb the state, and thus the fluctuations of work will generically depend on the particular measurement scheme which is being used.

The standard approach to estimate the fluctuations of work is the two projective measurement (TPM) scheme (TLH07). The TPM scheme consists on two projective energy measurements, one performed at the beginning and one at the end of the process. This scheme successfully characterises the process dependent nature of work, which is best illustrated by the fact that it allows for the generalisation Jarzynski-Crooks classical relations to the quantum regime. However, the measurements performed are invasive, as the first one destroys any quantum coherence in the state. This prevents the possibility of studying the thermodynamics of coherent processes: Even if the posterior evolution of the state is coherent, the first measurement prevents quantum interference effects - which are at the core of quantum physics. This raises the question whether there exist other measurement schemes that can successfully generalise the results of classical thermodynamics -in particular the celebrated Jarzynski-Crooks fluctuation theorems- and at the same time describe coherent transformations. Understanding to what extent this is possible, and suggesting a new measurement scheme to do so, is the central aim of this chapter.

Besides the TPM scheme, other protocols have been considered for estimating the fluctuations of work, (most of them) leading to different distributions and average values. In particular, continuous measurements of the system have been studied in (VWT15), measurements of work as an operator in the Heisenberg picture in (AN05a), and measurements through an ancillary system in (RCP14) -see, also, in a the framework of the resource theory of thermodynamics, the recent works (Abe16; AMOP16). The purpose of this work is to go beyond specific (albeit physically motivated) measurement schemes and take a more general approach, by considering *all* measurement schemes compatible with two minimal requirements: (i) agreement with the TPM scheme for states with no coherence, and (ii) agreement with the first law of thermodynamics at the level of average quantities for all states.

When considered individually, both requirements can be satisfied by distinct definitions of work. The TPM scheme satisfies (i) but not (ii) for coherent states because the first measurement is invasive; and the definition of work in (AN05a) satisfies (ii) but does not properly account for the fluctuations, and hence fails to satisfy (i). Attempts to satisfy both requirements simultaneously have been performed in (All14; SG15), but the corresponding distribution for work suffers from negative (quasi) probabilities (All14; SG15). Our first result is showing in full generality that there exists no measurement scheme that can simultaneously satisfy (i) and (ii). We show this result be considering both individual and collective measurements, in which a measurement is applied on several copies of the state that are independently undergoing the same process.

Although no measurement can satisfy (i) and (ii) exactly, collective measurements do provide a promising way to describe quantum fluctuations of work, as they can satisfy the two requirements with a better approximation that standard measurements to estimate work. In particular, we construct a measurement scheme, which acts on two copies of the state, that is able to describe a whole range of coherent transformations and is compatible with the results of the TPM scheme for diagonal states.

This Chapter is structured as follows. In Sec. 5.2, we describe the TPM scheme, and highlight its limitations for describing coherent processes. In Sec. 5.3, following (RCP14), we show how the TPM scheme can be described as a POVM. In Secs. 5.4, 5.5 and 5.6, we present one of our main results, which takes the form of a no-go theorem: There is no measurement scheme that can simultaneously agree with the TPM scheme for diagonal states in the energy basis and agree with the first law of thermodynamics for all states. In Secs. 5.7 and 5.8, we present the second main result: A new measurement scheme to approximately describe the fluctuations of work in coherent processes.

5.2. The two projective measurement scheme

Let us first briefly introduce the two projective measurement scheme to estimate the fluctuations of work in quantum systems (TLH07). This scheme was introduced in order to characterise the fluctuations of work of a thermally isolated quantum system ρ evolving under an auxiliary time dependent field- the results can be formally extended to the case of general open quantum systems (CTH09). During the process, the Hamiltonian of ρ is externally varied, and the evolution of ρ is described by a unitary operator U. The process can be simply described as,

$$\begin{aligned} H &\rightarrow H^{(f)} \\ \rho &\rightarrow U\rho U^{\dagger} \end{aligned} \tag{5.1}$$

where H ($H^{(f)}$) corresponds to the initial (final) Hamiltonian, and ρ ($U\rho U^{\dagger}$) to initial (final) state. Let us explicitly write

$$\begin{aligned} H &= \sum_i E_i |i\rangle\langle i| \\ H^{(f)} &= \sum_i E_i^{(f)} |i^{(f)}\rangle\langle i^{(f)}| = \sum_i E_i^{(f)} V|i\rangle\langle i|V^{\dagger}, \end{aligned} \tag{5.2}$$

where note that we have introduced the unitary operator V, which transforms the Hamiltonian basis,

$$|i^{(f)}\rangle = V|i\rangle. \tag{5.3}$$

Notice that we restrict ourselves, for clarity of the discussion, to finite dimension Hamiltonians with discrete spectra, but the reader should take into account that the generalisation to continuous spectra is straightforward (see e.g. (TLH07)).

Now, the first step of the protocol consists of a projective measurement of the energy on ρ. This yields $|i\rangle$ with probability $\langle i|\rho|i\rangle$. Only then the process is implemented, and the postselected state $|i\rangle$ evolves according to the unitary operation U. Finally, a projective energy measurement with respect to the final Hamiltonian is performed on the final state, yielding $|j^{(f)}\rangle$ with probability $|\langle j^{(f)}|U|i\rangle|^2$. To this realisation of the experiment, a work value

$$W^{(ij)} = E_i - E_j^{(f)} \tag{5.4}$$

is assigned, with corresponding probability

$$p^{(ij)} = \rho_{ii}\, p_{i,j}, \tag{5.5}$$

where

$$p_{i,j} = |\langle j^{(f)}|U|i\rangle|^2 = |\langle j|V^\dagger U|i\rangle|^2. \tag{5.6}$$

The whole probability distribution for work is obtained as,

$$P(W) = \sum_{ij} \delta(W - W^{(ij)}) p^{(ij)} \tag{5.7}$$

where δ is the Kronecker delta.

It is interesting to compare the results obtained through this work measurement scheme with those of the definition of average work introduced in Sec. 2.1.1 and used throughout the rest of this thesis. Within the TPM scheme, the average work is given by,

$$\begin{aligned}\langle W\rangle_{\text{TPM}} &= \sum_W WP(W) = \sum_{ij} p^{(ij)} W^{(ij)} \\ &= \sum_i \rho_{ii} E_i - \sum_{ij} \rho_{ii} p_{i,j} E_j^{(f)} \\ &= \sum_i \rho_{ii} E_i - \sum \rho_{ii} E_j^{(f)} U_{ki} U_{li}^* V_{lj} V_{kj}^* \end{aligned} \tag{5.8}$$

On the other hand, the average work according to (6.3) is given by,

$$\begin{aligned}\langle W\rangle &= \text{Tr}\left(\rho H^{(0)}\right) - \text{Tr}\left(U\rho U^\dagger H^{(f)}\right) \\ &= \sum_i \rho_{ii} E_i - \sum \rho_{im} E_j^{(f)} U_{ki} U_{lm}^* V_{lj} V_{kj}^* \end{aligned} \tag{5.9}$$

Notably, the two expressions become the same if ρ is a *diagonal* state. Indeed, introducing the dephasing operation $D[...]$, which dephases ρ in the energy basis defined by $|i\rangle$, we obtain that,

$$\begin{aligned}\langle W\rangle &= \text{Tr}\left(\rho H^{(0)}\right) - \text{Tr}\left(U\rho U^\dagger H^{(f)}\right) \\ \langle W\rangle_{\text{TPM}} &= \text{Tr}\left(\rho H^{(0)}\right) - \text{Tr}\left(UD(\rho)U^\dagger H^{(f)}\right) \\ \langle W\rangle - \langle W\rangle_{\text{TPM}} &= \text{Tr}\left(U(D(\rho) - \rho)U^\dagger H^{(f)}\right) \end{aligned} \tag{5.10}$$

Clearly, the two expressions become the same for states with no coherence in the energy basis, i.e., for $D(\rho) = \rho$. In fact, at the average level, the TPM scheme can be described as,

$$\rho \longrightarrow D(\rho) \longrightarrow UD(\rho)U^\dagger \longrightarrow D(UD(\rho)U^\dagger) \tag{5.11}$$

where $D(...)$ is a dephasing operator in the energy basis. In this form, it becomes clear that the TPM scheme does not describe quantum coherent processes, as the work fluctuations are computed on the process $D(\rho) \longrightarrow UD(\rho)U^{\dagger}$.

5.3. Fluctuations of work and POVMs

In order to characterize the fluctuation of work, let us assume that the fluctuations of work can be characterised by a real random variable W, to which a probability distribution $P(W)$ can be assigned.[1] In quantum physics, such a $P(W)$ can only be estimated through a measurement process, which in turn can be always described by a generalized quantum measurement (a POVM). Indeed, it is important to note that any measurement scheme, possibly consisting of many different measurements, can always be described by a POVM.

A POVM is a set of positive operators $\{M^{(W)}\}$'s, which satisfy

$$\begin{aligned} M^{(W)} &\geq 0, \\ \sum_W M^{(W)} &= 1. \end{aligned} \tag{5.12}$$

Each possible value of work W is associated with an operator $M^{(W)}$, so that the probability to obtain W can be computed through

$$P(W) = \mathrm{Tr}(\rho M^{(W)}). \tag{5.13}$$

Only recently, it was noted in (RCP14) that the TPM scheme can be described as a POVM, which is given by,

$$M^{(W)}_{\mathrm{TPM}} = \sum_{ij} \delta(W - (E_i - E_j^{(f)}))p_{i,j}|i^{(0)}\rangle\langle i^{(0)}|. \tag{5.14}$$

In the case where the possible values of work $E_i - E_j^{(f)}$ are non-degenerate, we can introduce the operators $M^{(ij)} \equiv M^{(E_i - E_j^{(f)})}$, and the TPM scheme then can be expressed simply as,

$$M^{(ij)}_{\mathrm{TPM}} = p_{i,j}|i^{(0)}\rangle\langle i^{(0)}|. \tag{5.15}$$

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[1] Note that in the rest of the thesis we have used W to design average work, whereas here it becomes a fluctuating quantity. In this chapter we shall use $\langle W\rangle$ to determine the average work.

Clearly, both constructions satisfy the conditions (5.12).

As we have discussed, this POVM successfully characterises the fluctuations of work for diagonal states, but tells us very little about coherent processes. Our objective is to explore other possible POVM that can also estimate the fluctuations of work in a meaningful way, and at the same time allow to characterise the fluctuations in coherent processes. As in (5.14), we expect that the operators $M^{(W)}$ are functions of the process, $M^{(W)} = f(U, H, H_f)$, but do not depend on the initial state ρ. Indeed, we would like to estimate the work done in a process without knowledge of the initial state.

5.4. Minimal requirements to describe the fluctuations of work

In this section we present two minimal requirements that a measurement scheme for characterizing the fluctuations of work should desirably satisfy. They consist of,

(i) agreement with the TPM scheme for states with no coherence (in the energy basis), and

(ii) agreement with the first law of thermodynamics at the level of average quantities for all states.

By imposing requirement (i), we ensure that we recover all probability distributions from the well known TPM scheme, particularly the fulfillment of the fluctuation theorems. Requirement (ii) is meant to give a minimal condition for the extension of this scheme to coherent states. In this sense, notice that we limit this condition to the average energy, which is operationally well defined for coherent states.

We can now express these two requirements in detail by using our previous considerations on POVMs. The first one simply states that,

$$\mathrm{Tr}(\rho_{\mathrm{diag}} M^{(W)}) = \mathrm{Tr}(\rho_{\mathrm{diag}} M^{(W)}_{\mathrm{TPM}}) \qquad \forall \rho_{\mathrm{diag}}, W \tag{5.16}$$

where $M^{(W)}_{\mathrm{TPM}}$ is given in (5.14), ρ_{diag} is any state that can be expressed as

$$\rho_{\mathrm{diag}} = \sum_i p_i |i\rangle\langle i|. \tag{5.17}$$

If no degeneracies exist in the values of work, we can associate to each energy transition a operator operator, $M^{(ij)} \equiv M^{(E_i - E_j^{(f)})}$, and then condition can be decomposed into (5.16),

$$\mathrm{Tr}(\rho_{\mathrm{diag}} M^{(ij)}) = \rho_{ii}\, p_{i,j} \qquad \forall \rho_{\mathrm{diag}}, i, j \tag{5.18}$$

$$\mathrm{Tr}(\rho_{\mathrm{diag}} M^{(W)}) = 0 \qquad \forall \rho_{\mathrm{diag}}, \quad \text{if} \quad M^{(W)} \neq M^{(ij)}, \forall i, j. \tag{5.19}$$

According to our definitions of work and heat in Sec. 2.1.1, agreement with the first law simply means that,

$$\langle W \rangle = \mathrm{Tr}(\rho H) - \mathrm{Tr}\left(U \rho U^{\dagger} H_f\right), \qquad \forall \rho \tag{5.20}$$

with $\langle W \rangle = \sum_W W P(W)$. As we have stressed in Sec. 5.2, the TPM scheme agrees with this expression for the average work as long as the initial state has no energy coherence.

Finally, we note that the quantity (5.20) has been recently referred to as untouched work in (TH16), as it refers to the average work in absence of any back action from the measurement apparatus. However, it is important to note that there exist measurement schemes that can obtain (5.20), as we will now show. Of course, we would like our measurement scheme to change (5.20) as little as possible, in order to describe the process (5.1) with maximal precision.

5.5. Fundamental limitations for work measurements in coherent processes

In this section we will prove that there is no measurement scheme compatible simultaneously with requirements (i) and (ii). This result, together with the extension to global measurements in Sec. 5.6, is one of two main results of this Chapter.

We consider a POVM with operators $M^{(W)}$, where W may a priori take any real value. Now we can use condition (5.19) to limit such values. Indeed, by considering $\rho_{\mathrm{diag}} = |k\rangle\langle k|\ \forall k$, we obtain that

$$\langle k | M^{(W)} | k \rangle = 0 \quad \text{if} \quad W \neq E_i - E_j^{(f)}, \qquad \forall i, j, k. \tag{5.21}$$

Furthermore, from the positivity of $M^{(W)}$, it follows that, $\langle k | M_W | l \rangle = 0$ if $W \neq E_i - E_j^{(f)}$, $\forall i, j, k, l$. Therefore,

$$M^{(W)} = 0 \quad \text{if} \quad W \neq E_i - E_j^{(f)}, \tag{5.22}$$

and hence $P(W) = 0$ if $W \neq E_i - E_j^{(f)}$. Summarizing, from requirement (5.19) it follows that the only values that work can take are difference of energies.

Requirement (i) also sets the value of the diagonal elements of $M^{(ij)}$, where recall that $M^{(ij)} \equiv M^{(E_i - E_j^{(f)})}$. By again considering $\rho_{\text{diag}} = |k\rangle\langle k| \; \forall k$, we obtain from (5.18) that

$$\langle k|M^{(ij)}|k\rangle = \delta_{ik} p_{i,j} \tag{5.23}$$

Since there is only one non-zero diagonal element, the positivity of $M^{(ij)}$ implies that all off-diagonal elements are zero. Therefore, whenever no degeneracies exist in the values of $E_i - E_j^{(f)}$, requirement (i) completely sets the measurement operators $M^{(ij)}$ to

$$M^{(ij)} = p_{i,j} |i^{(0)}\rangle\langle i^{(0)}|, \tag{5.24}$$

which coincides with (5.24).

Consider now the requirement (ii). The average work of a certain process can be estimated as $\langle W\rangle_\rho = \sum_W \mathrm{Tr}(M^{(W)}\rho)W$. It will be convenient to introduce the operator

$$X = \sum_W W M^{(W)}, \tag{5.25}$$

so that $\langle W\rangle_\rho = \mathrm{Tr}\,(X\rho)$. Condition (5.20) implies that $\mathrm{Tr}\,(X\rho) = \mathrm{Tr}(\rho H) - \mathrm{Tr}\left(U\rho U^\dagger H_f\right)$, which, after a simple rearrangement reads,

$$\mathrm{Tr}\,(X\rho) = \mathrm{Tr}\left((H - U^\dagger H_f U)\rho\right), \qquad \forall\rho \tag{5.26}$$

which shows that

$$X = H - U^\dagger H_f U \tag{5.27}$$

is a solution. Since this must hold $\forall\rho$, the solution is unique. Note that this does not mean that the measurement scheme, i.e. the set of M_{W} are fixed. There are many possible combinations of $M^{(\mathrm{W})}$ such that $X = (U^\dagger H_f U - H)$ and $\sum_{\mathrm{W}} M_{\mathrm{W}} = 1$. However, it is easy to see that in most cases they are not compatible with (5.24). We show that by considering a particular process.

Consider a two level system ρ and an initial Hamiltonian $H = \epsilon|1\rangle\langle 1|$ and a final one $H_f = \delta|1\rangle\langle 1|$. The process is described by the following unitary operation

$$U = |0\rangle\langle +| + |1\rangle\langle -|, \tag{5.28}$$

with $|+\rangle = (|0\rangle + |1\rangle)/\sqrt{2}$, $|-\rangle = (|0\rangle - |1\rangle)/\sqrt{2}$. Note that $U^{-1} = U$. Consider now a set of POVMs $M^{(W)} = f(U, H, H_f)$. From (5.25), we find $X_{\text{(ii)}}$ as the operator associated with the average value of work, obtaining

$$X_{\text{(ii)}} = \epsilon|1\rangle\langle 1| - \delta|-\rangle\langle -|. \tag{5.29}$$

where we added the subindex (ii) to stress that it comes from requirement (ii). On the other hand, we can use expression (5.24) to determine the work operators compatible with requirement (i). This yields, $M^{(0,0)} = |0\rangle\langle 0|/2$, $M^{(0,1)} = |0\rangle\langle 0|/2$, $M^{(1,0)} = |1\rangle\langle 1|/2$, $M^{(1,1)} = |1\rangle\langle 1|/2$; and from (5.25) we obtain

$$X_{(\mathrm{i})} = \sum_{ij} M^{(ij)} = -\delta\frac{|0\rangle\langle 0|}{2} + (2\epsilon - \delta)\frac{|1\rangle\langle 1|}{2}. \tag{5.30}$$

Clearly, $X_{(\mathrm{i})} \neq X_{(\mathrm{ii})}$, which proves that there does not exist any set of $M^{(W)}$'s, or equivalently any measurement scheme, that can simultaneously satisfy conditions (i) and (ii) given the process described by (5.28).

5.6. Global Measurements

The previous result provides a fundamental limitation on our ability to characterize the fluctuations of work in quantum physics. If one wants to minimize the back action of the measurement apparatus, in order to preserve (5.20), one must renounce to a right description of the fluctuations of work; and viceversa. This was shown by considering arbitrary measurement schemes. In this section, we extend this no-go result to global measurements on many copies of the state. More precisely, we consider collective measurements on n copies of the state, each of them evolving independently through the same unitary process. The intuition behind is clear: By acting on several copies with fine-tuned measurements, the back action of the measurement apparatus can be drastically reduced. In order to study the capabilities of such collective strategies, as in the previous section, we do not focus on particular measurement schemes, but rather consider generic global measurements under requirements (i) and (ii). Again, POVM's are a powerful tool for this task.

When considering global measurements on n copies of the state, the operators $M_n^{(W)}$ will act on $\rho^{\otimes n}$ instead of ρ. In this case, requirement (i) can be expressed as,

$$\mathrm{Tr}(\rho_{\mathrm{diag}}^{\otimes n} M^{(ij)}) = \mathrm{Tr}(\rho_{\mathrm{diag}} M_{\mathrm{TPM}}^{(ij)}) \qquad \forall \rho_{\mathrm{diag}} \tag{5.31}$$

where $M_{\mathrm{TPM}}^{(ij)}$ is given by (5.15); and requirement (ii) reads as,

$$\mathrm{Tr}(\rho^{\otimes n} X) = \mathrm{Tr}\left(\rho H\right) - \mathrm{Tr}\left(U\rho U^{\dagger} H^{(f)}\right) \qquad \forall \rho \tag{5.32}$$

where $X = \sum_{ij} W^{(ij)} M^{(ij)}$. Notice that essentially the same restrictions are imposed on $M^{(ij)}$, which now live in a Hilbert space of dimension d^n instead of d -the dimension of ρ. This gives an enormous freedom to the measurement operators that was not present before.

Despite the large freedom to choose the $M^{(W)}$, we now show that there exist processes where requirements (i) and (ii) can not be simultaneously satisfied by any measurement scheme, even if n is arbitrarily large. For that, we consider unitary operations of the form,

$$U(\epsilon) = \sqrt{1-\epsilon^2}\mathbb{I} + \epsilon i \sigma_y \tag{5.33}$$

with $\epsilon > 0$, and cyclic processes, where $H^{(f)} = H = |1\rangle\langle 1|$. Let us introduce $\mathbf{k} = k_1 \cdots k_n$ an n-bit string, with $|\mathbf{k}| = \sum_i k_i$ being the Hamming weight (number of 1s) of the string. The states $|\mathbf{k}\rangle = |k_1\rangle \cdots |k_n\rangle$ run over all d^n energy eigenstates of the total Hamiltonian, $\sum_{j=1}^n H$. For the unitary (5.33), condition (5.31) can be then expressed as,

$$\sum_{\mathbf{k}} p_1^{|\mathbf{k}|} p_0^{n-|\mathbf{k}|} \langle \mathbf{k}| M^{(ij)} |\mathbf{k}\rangle = \epsilon^2 (\delta_{i0} p_0 + \delta_{i1} p_1) \tag{5.34}$$

where we took $\rho_{\text{diag}} = p_0|0\rangle\langle 0| + p_1 |1\rangle\langle 1|$. From this expression, it is clear that,

$$\langle \mathbf{k}| M^{(ij)} |\mathbf{k}\rangle \leq \epsilon^2 \qquad \forall \mathbf{k}. \tag{5.35}$$

Because the operators $M^{(ij)}$ must be positive, this condition implies that the (free) off-diagonal terms of $M^{(ij)}$ must satisfy,

$$\langle \mathbf{k}| M^{(ij)} |\mathbf{l}\rangle \leq \epsilon^2 \qquad \forall \mathbf{k}, \mathbf{l}. \tag{5.36}$$

Consider now the average work operator,

$$X = \sum_{ij} W^{(ij)} M^{(ij)} = M^{(01)} - M^{(10)} \tag{5.37}$$

and the state,

$$|+\rangle = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle). \tag{5.38}$$

We obtain the bound,

$$\left|\text{Tr}\left((|+\rangle\langle +|)^{\otimes n} X\right)\right| = \left| \frac{1}{2^n} \sum_{\mathbf{k},\mathbf{l}} \langle \mathbf{k}|X|\mathbf{l}\rangle \right| < 2^{n+1}\epsilon^2. \tag{5.39}$$

Let us know consider requirement (ii). We obtain that,

$$\langle W \rangle_\rho = \text{Tr}\left(\rho(H - U^\dagger H U)\right) = \epsilon^2(\rho_{11} - \rho_{00}) - 2\epsilon\sqrt{1-\epsilon^2}\text{Re}[\rho_{01}] \tag{5.40}$$

For the state (5.38),

$$\left|\langle W\rangle_{|+\rangle}\right| = \epsilon\sqrt{1-\epsilon^2} \tag{5.41}$$

Now, if we choose $\epsilon = 1/(n2^{n+1})$, we obtain, for n large enough

$$\left|\mathrm{Tr}\left((|+\rangle\langle+|)^{\otimes n}X\right)\right| < \frac{1}{n^2 2^{n+1}} < \frac{1}{n^2 2^{n+1}} \approx \left|\langle W\rangle_{|+\rangle}\right| \tag{5.42}$$

This finishes the proof: If ϵ in (5.33) is small enough, then there exists no measurement scheme compatible with (5.31) that can satisfy (5.32). This generalizes the previous no-go result to arbitrary collective measurements, i.e., measurements that act on a finite number of copies of ρ.

It is interesting to note that in the specific setting where the proof is built -the unitary $U(\epsilon)$ acting on a qubit system-, the value of ϵ for which the two requirements can not be satisfied decreases as n increases. This suggests that collective measurements, while are not able to fully characterize quantum fluctuations, can provide much better descriptions of them. This possibility is studied in detail in the next sections.

5.7. A measurement scheme for the characterization of the quantum fluctuations of work in qubit systems

In this section, together with our considerations in Sec. 5.8, we construct a measurement scheme on two copies of the state which can approximately describe the fluctuations of coherent processes.

Let us now exemplify the potential of collective measurements, by focusing on measurements performed on two copies of a qubit undergoing a coherent evolution. For simplicity, in this section we consider cyclic processes with

$$H = |1\rangle\langle 1|. \tag{5.43}$$

For ease of the argument, we also assume that we can differentiate the four possible transitions, so that a different measurement operator $M^{(ij)}$ is assigned to each of them. The general case is treated in the next section.

Let us first study which measurement set-ups are compatible with requirement (i). For cyclic processes, it implies that,

$$\mathrm{Tr}(\rho_{\mathrm{diag}}^{\otimes 2} M^{(ij)}) = \langle i|\rho_{\mathrm{diag}}|i\rangle\; |U_{ji}|^2, \qquad \forall\rho_{\mathrm{diag}} \tag{5.44}$$

$$\mathrm{Tr}(\rho_{\mathrm{diag}}^{\otimes 2} M^{(W)}) = 0, \quad \forall\rho_{\mathrm{diag}} \qquad \text{if} \qquad M^{(W)} \neq M^{(ij)} \tag{5.45}$$

where $M^{(ij)}$ can take four values: $M^{(00)}$, $M^{(01)}$, $M^{(10)}$, $M^{(11)}$ corresponding to the different energy transitions (from ground state to ground state, from ground state to excited, etc.). Firstly, from (5.45), and proceeding as in the previous sections, one easily obtains that the only non-zero $M^{(W)}$ are the four $M^{(ij)}$. Secondly, condition (5.44) sets the diagonal elements of $M^{(ij)}$. Indeed, by first considering $\rho_{\text{diag}} = |0\rangle\langle 0|$ and $\rho_{\text{diag}} = |1\rangle\langle 1|$, we obtain

$$\begin{aligned} \langle 0,0|M^{(0,0)}|0,0\rangle &= |U_{00}|^2 \\ \langle 1,1|M^{(0,0)}|1,1\rangle &= 0, \end{aligned} \tag{5.46}$$

and by considering $\rho_{\text{diag}} = p|0\rangle\langle 0| + (1-p)|1\rangle\langle 1|$, we arrive at,

$$p^2|U_{00}|^2 + p(1-p)\,\mathrm{Tr}\left(M^{(00)}(|01\rangle\langle 01| + |10\rangle\langle 10|)\right) = p|U_{00}|^2 \tag{5.47}$$

which implies,

$$\langle 01|M^{(00)}|01\rangle + \langle 10|M^{(00)}|10\rangle = |U_{00}|^2. \tag{5.48}$$

Summarising, we obtain that

$$\mathrm{diag}(M^{(00)}) = |U_{00}|^2\{1, 1-\alpha^{(0,0)}, \alpha^{(0,0)}, 0\} \qquad \alpha^{(0,0)} \in [0,1]. \tag{5.49}$$

Similarly, we obtain,

$$\begin{aligned} \mathrm{diag}(M^{(00)}) &= |U_{00}|^2\{1, 1-\alpha^{(00)}, \alpha^{(00)}, 0\} & \alpha^{(00)} &\in [0,1], \\ \mathrm{diag}(M^{(01)}) &= |U_{10}|^2\{1, 1-\alpha^{(01)}, \alpha^{(01)}, 0\} & \alpha^{(01)} &\in [0,1], \\ \mathrm{diag}(M^{(10)}) &= |U_{01}|^2\{0, \alpha^{(10)}, 1-\alpha^{(10)}, 1\} & \alpha^{(10)} &\in [0,1], \\ \mathrm{diag}(M^{(11)}) &= |U_{11}|^2\{0, \alpha^{(11)}, 1-\alpha^{(11)}, 1\} & \alpha^{(11)} &\in [0,1]. \end{aligned} \tag{5.50}$$

Because we have freedom on their choice, let us set $\alpha^{(00)} = \alpha^{(01)} = \alpha^{(10)} = \alpha^{(11)} = 0$. The off-diagonal terms of $M^{(ij)}$ are restricted by positivity constraints and by $\sum M^{(ij)} = \mathbb{I}$. Combining those constraints we obtain,

$$M^{(00)} = \begin{pmatrix} |U_{00}|^2 & -x & 0 & 0 \\ -x^* & |U_{00}|^2 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix},$$

$$M^{(01)} = \begin{pmatrix} |U_{10}|^2 & x & 0 & 0 \\ x^* & |U_{10}|^2 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix},$$

$$M^{(10)} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & |U_{01}|^2 & -y \\ 0 & 0 & -y^* & |U_{01}|^2 \end{pmatrix},$$

$$M^{(11)} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & |U_{11}|^2 & y \\ 0 & 0 & y^* & |U_{11}|^2 \end{pmatrix}$$

where $|x| \leq \min\{|U_{00}|^2, |U_{10}|^2\}$ and $|y| \leq \min\{|U_{01}|^2, |U_{11}|^2\}$. Let us now focus our attention on cyclic processes, for which only $M^{(10)}$ and $M^{(01)}$ have a non-zero ϵ work value. In this case, we obtain,

$$X_i = \sum_{ij} (E_i - E_j^{(f)}) M^{(ij)} = \epsilon \begin{pmatrix} -|U_{10}|^2 & -x & 0 & 0 \\ -x^* & -|U_{10}|^2 & 0 & 0 \\ 0 & 0 & |U_{01}|^2 & -y \\ 0 & 0 & -y^* & |U_{01}|^2 \end{pmatrix}$$

For a general initial state ρ,

$$\rho = \begin{pmatrix} \rho_{00} & \rho_{01} \\ \rho_{10} & \rho_{11} \end{pmatrix},$$

we obtain,

$$\mathrm{Tr}(X_i \rho^{\otimes 2}) = \left(-\rho_{00}|U_{10}|^2 + \rho_{11}|U_{01}|^2\right) - 2\epsilon(\rho_{00}\,\mathrm{Re}(\rho_{10}x) + \rho_{11}\,\mathrm{Re}(\rho_{10}y^*)) \tag{5.51}$$

We can identify two terms. The first one comes from the diagonal part of ρ, and hence corresponds to the average work as predicted by the TPM scheme. The second one comes from the coherent part of ρ, and it depends on x and y, the two free parameters in our measurement scheme. Those should be chosen so that requirement (ii) is satisfied.

Regarding requirement (ii), and again assuming cyclic processes with $H = \epsilon|1\rangle\langle 1|$, we obtain that the set of measurement operators $M^{(W)}$, with $X_{ii} = \sum_W W M^{(W)}$, should satisfy

$$\mathrm{Tr}(X_{ii}\rho^{\otimes 2}) = \mathrm{Tr}(\rho(H - U^\dagger H U)) = \left(-\rho_{00}|U_{10}|^2 + \rho_{11}|U_{01}|^2\right) - 2\,\mathrm{Re}(U_{11}U_{10}^*\rho_{10}) \tag{5.52}$$

The two expressions for the average work, (5.51) and (5.52), become identical if one takes $x = y^* = U_{11}U_{10}^*$. However, the values of x and y are subject to the positivity constraints $|x| \leq \min\{|U_{00}|^2, |U_{10}|^2\}$ and $|y| \leq \min\{|U_{01}|^2, |U_{11}|^2\}$. Generally, we can take

$$x = y^* = U_{11}U_{10}^* \frac{\min\{|U_{00}|^2, |U_{01}|^2, |U_{10}|^2, |U_{11}|^2\}}{|U_{11}||U_{10}|}, \tag{5.53}$$

which ensures positivity and that the difference between the average work and the estimated one is minimal.

Finally, it is important to stress that the measurement operators we constructed, determined by the choices of x and y, depend on U, but not on the specific state ρ. This is because one would like to use the same measurement scheme independently of the given state ρ.

5.7.1. An exemplary case

In order to illustrate the previous considerations, let us consider a specific coherent evolution given by,

$$\frac{|0\rangle + |1\rangle}{\sqrt{2}} \longrightarrow |0\rangle \tag{5.54}$$

More specifically, we consider the unitary given by $U = |0\rangle\langle +| + |1\rangle\langle -|$, with $|+\rangle = (|0\rangle + |1\rangle)/\sqrt{2}$, $|-\rangle = (|0\rangle - |1\rangle)/\sqrt{2}$, and consider the process to be cyclic with the initial (and final) Hamiltonian being $H = |1\rangle\langle 1|$. We will now compare the work fluctuations of this process as predicted by the TPM -which is equivalent to our measurement scheme when single copies are processed - with that predicted by collective measurement on two copies. Recall the definition of the transition probabilities,

$$p^{(ij)} = p_i p_{i,j} \tag{5.55}$$

with $p_{i,j} = |U_{ji}|^2$

Predictions by the TPM. Applying the TPM scheme we obtain the following values for the probabilities of work,

- $p^{(00)} = 1/4$,
- $p^{(01)} = 1/4$,
- $p^{(10)} = 1/4$,
- $p^{(11)} = 1/4$.

where $p^{(ij)}$ are the probabilities associated with the transitions $|i\rangle \to |j\rangle$. These predictions have little resemblance to the quantum process described in (5.54). For example, according to the TPM scheme, the state ends at $|1\rangle$ with probability 1/2, whereas from (5.54) one would expect this probability to be 0. This does not imply that the predictions of the TPM are incorrect, it simply shows that the back reaction of the apparatus is very important.

Predictions by a collective measurement of two copies. Now we take our measurement scheme defined through the operators $M^{(ij)}$ with x, y given in (5.53). A direct calculation yields,

- $p^{(00)} = 1/2$,
- $p^{(01)} = 0$,
- $p^{(10)} = 1/2$,
- $p^{(11)} = 0$.

These probabilities are much closer to the *untouched* process (5.54). In this case, the back action of the apparatus is small and the coherent nature of the process is preserved.

This simple example shows how our measurement scheme allows for the exact description of the fluctuations of work in some quantum coherent processes. Remarkably, this is done by keeping the process nature of work inherited from classical thermodynamics -by construction, the measurement scheme agrees with the results of the TPM scheme whenever the state is non-coherent.

5.8. Generalisation to arbitrary systems

In this section we generalise our previous considerations to generic qudit systems: We will construct a collective measurement on two copies in order to characterise coherent processes. We will not restrict ourselves to cyclic processes, and consider totally generic evolutions and Hamiltonian transformations, as in (5.1). From (5.2), it will be convenient to introduce the unitary operator,

$$W = V^{\dagger}U. \tag{5.56}$$

Consider the work operators $M^{(ij)}$. Inspired by our considerations in the last section, we choose them to take the form,

$$M^{(ij)} = |i\rangle\langle i| \otimes T^{(ij)} \tag{5.57}$$

where we note that the $T^{(j)}$'s are functions of the elements of U and will be determined later. The operators $M^{(ij)}$ forming a POVM implies that

$$\sum_j T^{(ij)} = \mathbb{I}, \tag{5.58}$$

$$T^{(ij)} \geq 0. \tag{5.59}$$

On the other hand, requirement (i) implies that,

$$\mathrm{Tr}\left(\rho_{\mathrm{diag}} T^{(ij)}\right) = |W_{ji}|^2, \qquad \forall \rho_{\mathrm{diag}}. \tag{5.60}$$

This suggests the following ansatz for the operators $T^{(ij)}$,

$$T^{(ij)} = |W_{ji}|^2 \mathbb{I} + A^{(ij)}_{\mathrm{offd}} \tag{5.61}$$

where $A^{(ij)}_{\mathrm{offd}}$ is a matrix made up of off diagonal elements only. We have freedom to choose $A^{(ij)}_{\mathrm{offdiag}}$ up to the constraints (5.58) and (5.59).

Now, by defining,

$$X_{(\mathrm{i})} \equiv \sum_{ij} (E_i - E^{(f)}_j) M^{(ij)} \tag{5.62}$$

we can compute the average work obtained through this measurement scheme as, $\mathrm{Tr}(\rho^{\otimes 2} X_i)$,

$$\mathrm{Tr}(\rho^{\otimes 2} X_i) = \sum_{ij} E_i \, \mathrm{Tr}\left(\rho^{\otimes 2} M^{(ij)}\right) - \sum_{ij} E^{(f)}_i \, \mathrm{Tr}\left(\rho^{\otimes 2} M^{(ji)}\right) \tag{5.63}$$

Let us compute each term individually. For the first one we obtain,

$$\sum_{ij} E_i \, \mathrm{Tr}\left(\rho^{\otimes 2} M^{(ij)}\right) = \sum_i E_i \, \mathrm{Tr}\left(\rho^{\otimes 2} |i\rangle\langle i| \otimes \mathbb{I}\right) = \sum_i E_i \langle i|\rho|i\rangle, \tag{5.64}$$

and for the second,

$$\begin{aligned} \sum_{ij} E^{(f)}_i \, \mathrm{Tr}\left(\rho^{\otimes 2} M^{(ji)}\right) &= \sum_i E^{(f)}_i \, \mathrm{Tr}\left(\rho^{\otimes 2} \left(\sum_j |j\rangle\langle j| \otimes T^{(ji)}\right)\right) \\ &= \sum_i E^{(f)}_i \sum_j \langle j|\rho|j\rangle \, \mathrm{Tr}\left(\rho T^{(ji)}\right) \\ &= \sum_i E^{(f)}_i \sum_j \langle j|\rho|j\rangle \left(|W_{ij}|^2 + \mathrm{Tr}(\rho A^{(ji)}_{\mathrm{offd}})\right) \end{aligned} \tag{5.65}$$

On the other hand, we can compute the average work in absence of back action of the apparatus (i.e., requirement (ii)),

$$\begin{aligned}\mathrm{Tr}(\rho X_{(\mathrm{ii})}) &= \mathrm{Tr}\left(\rho(H - U^\dagger H^{(f)} U)\right)\\ &= \sum_i E_i \langle i|\rho|i\rangle - \sum_i E_i^{(f)} \sum_{jk} W_{ij} W_{ik}^* \langle j|\rho|k\rangle\\ &= \sum_i E_i \langle i|\rho|i\rangle - \sum_i E_i^{(f)} \left(\sum_j \langle j|\rho|j\rangle |W_{ij}|^2 - \sum_{l\neq k} W_{il} W_{ik}^* \langle l|\rho|k\rangle \right),\end{aligned} \tag{5.66}$$

where in the last equality we reordered some terms and changed some indexes for convenience. From inspecting equations (5.65) and (5.66), we infer that the choice,

$$A^{(ji)} = \sum_{l\neq k} W_{il} W_{ik}^* |k\rangle\langle l| \tag{5.67}$$

leads to $\mathrm{Tr}(\rho X_{(\mathrm{ii})}) = \mathrm{Tr}(\rho^{\otimes 2} X_{(\mathrm{i})})$, as desired. Explicitly, we obtain that the operators $T^{(ij)}$ take the form

$$T^{(ij)} = |W_{ji}|^2 \mathbb{I} + \sum_{l\neq k} W_{jl} W_{jk}^* |k\rangle\langle l| \tag{5.68}$$

However, at the moment this is just a formal choice: In order to obtain a proper quantum measurement the conditions (5.58) and (5.59) need to be satisfied. Regarding (5.58), we obtain,

$$\begin{aligned}\sum_j T^{(ij)} &= \sum_j |W_{ji}|^2 \mathbb{I} + \sum_{l\neq k} \left(\sum_j W_{jl} W_{jk}^* \right) |k\rangle\langle l|\\ &= \mathbb{I} + \sum_{l\neq k} \delta_{kl} |k\rangle\langle l| = \mathbb{I},\end{aligned} \tag{5.69}$$

where we used that $W^\dagger W = \mathbb{I}$. Hence, our choice naturally satisfies constraint (5.58). The positivity constraint (5.59) will depend on the particular choice for U. In fact, as we have shown in Sec. 5.6, there exist choices for which the operators cannot be positive. In such cases, the matrix $A^{(ij)}$ needs to be chosen as close as possible to (5.67), in such a way that the back action of the apparatus is minimised. This can be implemented by introducing a parameter α, and defining

$$T_\alpha^{(ij)} = |W_{ji}|^2 \mathbb{I} + \alpha \sum_{l \neq k} W_{jl} W_{jk}^* |k\rangle\langle l| \tag{5.70}$$

where $\alpha \in [0,1]$ is chosen according to $\alpha = \max_\beta(\beta \mid T_\beta^{(ij)} \geq 0 \, \forall i,j)$.

Summarizing, our measurement scheme to characterize the fluctuations of work takes the form

$$M^{(ij)} = |i\rangle\langle i| \otimes \left(|W_{ji}|^2 \mathbb{I} + \alpha \sum_{l \neq k} W_{jl} W_{jk}^* |k\rangle\langle l| \right). \tag{5.71}$$

In particular, the probability of obtaining the transition $E_j^{(f)} - E_i$ is given by $\mathrm{Tr}(\rho^2 M^{(ij)})$. The construction (5.71) is the second main result of this Chapter, and following we show its usefulness and give an interpretation of the scheme.

5.8.1. Application: Characterisation of the fluctuations induced by fully coherent operations

We now apply our previous general considerations to processes that can generate maximal coherence, or conversely extract work from maximally coherent states. In particular, we consider unitary operations of the form,

$$U = \frac{1}{\sqrt{d}} \sum_{j,k}^{d-1} e^{-\frac{2\pi i}{d} jk} |j\rangle\langle k| \tag{5.72}$$

where d is the dimension of the Hilbert space. We also consider cyclic processes. In this case, we can obtain the operators $T^{(ij)}$ in (5.68), and they take the form

$$\begin{aligned} T^{(ij)} &= \frac{1}{d}\mathbb{I} + \frac{1}{d} \sum_{l \neq k}^{d-1} e^{-\frac{2\pi i}{d} j(l-k)} |k\rangle\langle l| = \frac{1}{d} \sum_{l,k=0}^{d-1} e^{-\frac{2\pi i}{d} j(l-k)} |k\rangle\langle l| \\ &= U|j\rangle\langle j|U^\dagger, \end{aligned} \tag{5.73}$$

Clearly, in this case the choice (5.67) defines proper measurement operators, and hence $\alpha = 1$ in the measurements (6.41). Recall that this implies that the second requirement (ii) can be satisfied exactly in this process. The measurement operators can be written as,

$$M^{(ij)} = |i\rangle\langle i| \otimes U|j\rangle\langle j|U^\dagger. \tag{5.74}$$

This scheme can be applied to any initial state ρ, and it allows for the characterisation of the fluctuations of work in processes induced by (5.72). This is achieved by performing different measurements on the two copies, hence minimising the back action of the apparatus. Note that these considerations are a generalisation of the example discussed in Sec. 5.7.1.

5.8.2. Interpretation of the measurement scheme

Let us first discuss the particular case of the coherent evolution in (5.72), in which case the measurement is given by (5.74). This scheme has a simple interpretation: Given a pair of two states $\rho^{\otimes 2}$, we perform a projective measurement of the energy to ρ; whereas the other copy first evolves as $U\rho U^{\dagger}$, and only then a projective measurement of the energy is made. Notice that, in this case, the two measurement are completely independent.

The interpretation of the general measurement, given by (5.57) and (6.41), which can be applied to any process, is slightly more subtle. To the first copy, a projective measurement of the energy is always made. Now, depending on the outcome of this measurement, a different measurement will be performed on the other ρ, which is given by (6.41) and depends on the value of the parameter α.

5.9. Concluding remarks

In this chapter we have explored the possibility of describing the fluctuations of work in quantum coherence processes. We have first provided a no-go result: There is no measurement scheme to estimate the fluctuations of work that can be in agreement simultaneously with (i) the classical fluctuation theorems (i.e., the TPM scheme) and (ii) the first law of thermodynamics (as expressed by the relation (5.20)). This result applies even when collective measurements are considered.

Secondly, we have used collective measurement on two copies of in order to obtain measurement processes that can, to a reasonably good approximation, agree simultaneously with (i) and (ii). In particular, we constructed a measurement scheme, which acts on two copies of the state, that is able to describe a whole range of coherent transformations and is compatible with the results of the TPM scheme for states with no coherence in the energy basis.

6. Extractable Work from Correlations

6.1. Introduction

In this chapter we come back to the problem of work extraction from quantum systems. The setting we consider is similar to the one described in Chapter 3 : Extracting work via highly controlled (unitary) operations from thermally isolated quantum systems. In Chapter 3, we showed that global operations are capable of extracting more work than local ones, as a state can be locally passive but globally not. The only case where global operations do not provide an advantage is that of a collection of (independent) Gibbs states at the same temperature. We termed such states *completely passive.* In fact, two conditions are required for complete passivity,

- local Gibbs states at the same temperature,
- independence of the local states (i.e., no correlations between them).

In chapter 1, we relaxed the first condition, and studied the extractable work from products of passive-but-not-thermal states. The aim of this chapter is to relax the second condition instead, and hence study the extractable work from purely correlations.

Our first result is to show that, if no restriction on the global state is made, then it is possible to store in the system the maximal amount of work compatible with the requirement that the reduced states are thermal. In other words, at the end of the protocol, the system is left in the ground state and, thus, all energy has been extracted. Notably this is possible thanks to quantum entanglement. It is then natural to ask if the same amount of work can be stored using a separable, or even a purely classical state diagonal states. We will see that, although the amount of work that can be stored in unentangled states is strictly smaller than the amount that can be stored in entangled states for any finite n, the gain decreases with the size of the system and in the thermodynamic limit ($n \to \infty$) purely classical states already become optimal. In fact, quantum resources offer a significant advantage only for small n, while neither entanglement nor energy coherences are needed for optimal work storage in the thermodynamic limit. We also consider additional natural constraints on the global state, such as limiting the entropy or requiring the decohered (classical) version of the state to be thermal, and investigate the role of quantum coherence and entanglement in these cases.

We also show that our results are applicable in the scenario where the system has an access to a thermal bath. There the connection between work extraction and correlations have been studied before (OHHH02; Zur03; JJR12; DL09; DRRV11). Given access to global operations on the subsystems, the extractable work is proportional to the mutual information (OHHH02; JJR12). That is, only the strength of the correlations is relevant, and not the type (i.e. quantum or classical). Here, in contrast, we show that when the bath (a macroscopic object) is not available and one has only a few subsystems, quantum correlations do provide a sizeable advantage. This brings new insights in the quantum-to-classical transition in thermodynamics.

Finally, we also compute the fluctuations of work in processes where the initial state is entangled. We show that entanglement not only modifies the average extractable work, but also modifies the probability of each single work values. Here the considerations of Chapter 5 become extremely useful, as they allow to deal with coherent states.

The results of this Chapter are original and can be found in (PLHH$^+$15a) (except for Sec. 6.7).

6.2. Framework

The framework we use is the same used in Chapter 3. We consider an isolated quantum system which consists of n d-level subsystems. The local Hamiltonian

$$h = \sum_a E_a |a\rangle\langle a| \tag{6.1}$$

is taken to be the same for each subsystem and, without loss of generality, it is assumed that the ground state energy is zero. We consider the situation where there is no interaction Hamiltonian between the subsystems, such that the total Hamiltonian H is simply the sum of the individual local Hamiltonians

$$H = \sum_i h_i . \tag{6.2}$$

As a set of operations for work extraction, we consider all unitary operations U. The extractable work W reads,

$$W = \mathrm{Tr}\left(\rho H\right) - \mathrm{Tr}\left(U \rho U^\dagger H\right) . \tag{6.3}$$

and is maximized by (2.22):

$$W_{\max} = \mathrm{Tr}(\rho \mathrm{H}) - \mathrm{Tr}(\rho^{\text{passive}} \mathrm{H}) \tag{6.4}$$

ρ^{passive} is the passive state with the same spectrum of ρ. Equation (6.4) defines the energy that can be potentially extracted from the state via cyclic hamiltonian (unitary) processes. This quantity in this chapter, and we refer to it as *extractable work, stored work* or *work content.*

We focus on the subset of all possible states of the system comprised by *locally thermal* states. That is, all ρ such that the reduced state of subsystem i satisfies

$$\rho_i = \mathrm{Tr}_{\bar{i}} \rho = \tau_\beta \tag{6.5}$$

for all i, where $\mathrm{Tr}_{\bar{i}}$ denotes the partial trace over all subsystems except subsystem i. Here τ_β is the thermal state of the subsystem at (a fixed but arbitrary) inverse temperature $\beta = 1/T$,

$$\tau_\beta = \frac{1}{\mathcal{Z}} e^{-\beta h}, \tag{6.6}$$

where $\mathcal{Z} = \mathrm{Tr}\, e^{-\beta h}$ is the partition function.

Apart from understanding how to exploit the general correlations to store work in the system, we also study the particular role of entanglement and energy coherences in these processes. We consider three natural sets of correlated states: (i) arbitrary states, thus including entangled ones, (ii) separable states and a subset of them: (iii) states diagonal in the product energy eigenbasis. We will study work extraction for these three different sets of correlated quantum states.

Before proceeding further, a comment is in order. In the previous chapter we showed that any scheme to measure the fluctuations of work will fail to achieve the average expression (6.3) for all initial states ρ and processes U. This limitation is particularly relevant for coherent and entangled states, which are of fundamental importance here. In Sec. 6.7, we discuss these subtleties, and in particular show that using the scheme devised in Sec. 5.8 we can describe the fluctuations of work extracted from an entangled state.

6.3. Extractable work from correlations

If ρ is locally thermal (6.5), and since H is a sum of local Hamiltonians, the first term of the right hand side of (6.4) is fixed and is given by

$$\mathrm{Tr}\,(\rho H) = n E_\beta, \tag{6.7}$$

where

$$E_\beta = \mathrm{Tr}(\tau_\beta h) \tag{6.8}$$

is the average energy of the local thermal state. Note also that given our convention that the ground state has zero energy, the second term of the right hand side of (6.4), that is, the final average energy, is always nonnegative. This implies that the extractable work is upper bounded by

$$W_{\max} \leq nE_\beta. \tag{6.9}$$

This bound is attainable if and only if the final state is the ground state, denoted by $|0\rangle^{\otimes n}$.

Quantum correlations are capable of making all the energy in the system available for extraction in the form of work, as they allow saturating the bound (6.9). Observe that the state

$$|\phi\rangle = \frac{1}{\sqrt{\mathcal{Z}}}\sum_{a=0}^{d-1} e^{-\frac{\beta E_a}{2}}|a\rangle^{\otimes n}. \tag{6.10}$$

is locally thermal, i.e., such that $\mathrm{Tr}_{\bar{i}}|\phi\rangle\langle\phi| = \tau_\beta$ for all i. Moreover, since it is pure, there exists a unitary matrix U such that $U|\phi\rangle = |0\rangle^{\otimes n}$. Thus all the energy nE_β can be extracted from state $|\phi\rangle$ and $W_{\max} = nE_\beta$.

It is clear that the state (6.10) is entangled. Hence it is natural to ask whether the amount of extractable work would change if we restrict ourselves to separable, or even classical states. If this is the case, then entanglement is necessary for optimal work extraction.

6.4. Extractable work from separable and classical states

A simple argument shows that separable states, contrary to entangled, do not allow for maximal work extraction. Separable states have the property that the global entropy is greater than all the local entropies (NC00). Now, if the system is initially in a separable state ρ, then $S(\rho) \geq S(\tau_\beta)$. This condition, first of all, indicates that the global state cannot be pure, implying that the bound (6.9) cannot be reached by separable states. So, what is the best that classical correlations can do?

A state that is separable and saturates the entropy bound $S(\rho) \geq S(\tau_\beta)$ is given by,

$$\rho_{\mathrm{sep}} = \frac{1}{\mathcal{Z}}\sum_{a=0}^{d-1} e^{-\beta E_a}|a\rangle\langle a|^{\otimes n}, \tag{6.11}$$

which is simply the state (6.10) after being dephased in the (global) energy eigenbasis. Furthermore, in Ref. (PLHH^{+}15a) it is shown that this is the separable state with the maximal extractable work (in particular, see Appendix A of (PLHH^{+}15a)). The extractable work from (6.11), W_{sep}, is found, as before, by finding its associated passive state, and then computing the average energy difference, see (6.4). Since ρ_{sep} is already diagonal (with d non-zero eigenvalues), it is only necessary to rearrange these non-zero eigenvalues to the lowest possible energy levels. Let us assume that $n \geq d-1$, (i.e. that we are in the regime of sufficiently many subsystems[1]). The $d-1$ largest eigenvalues can then simply be moved into the first excited subspace (with energy E_1), giving

$$W_{\text{sep}} = nE_\beta - E_1(1 - \mathcal{Z}^{-1}). \tag{6.12}$$

Note also that ρ_{sep} has no coherences, which means that diagonal and separable states have the same capacity.

Moreover, as the number of subsystems, n, increases, we see that W_{sep} and W_{max} become essentially the same: $W_{\text{sep}}/W_{\text{max}} = 1 - \mathcal{O}\left(n^{-1}\right)$ (see Fig. 6.1). This shows that, in the thermodynamic limit ($n \to \infty$), the difference between the extractable work from an entangled state and from a diagonal one vanishes, hence quantum coherences and entanglement play essentially no role here. However, for finite n there will always be a difference. In particular, in the regime of n relatively small, the ability to store work in entanglement offers a significant advantage (see Fig. 6.1).

6.5. Extractable work from states with fixed entropy

The previous results can be intuitively understood from entropy considerations. When the correlations in the state are not restricted, it is possible to satisfy the requirement of local thermality with pure entangled states, therefore attaining optimal work extraction. When the state is separable, the global entropy of the state cannot be zero as it is lower bounded by the local entropy and optimal work extraction becomes impossible. Note also that the separable state optimal for work extraction (6.12) has global entropy equal to the local one, which means that its global entropy does not scale with the number of subsystems. In other words, its entropy per subsystem tends to zero with the number of subsystems, which intuitively explains why the state tends to be optimal in this limit.

---

[1] For qubits or qutrits ($d = 2$ and 3, respectively) any ensemble is big enough, since in both cases $d - 1 \leq 2$.

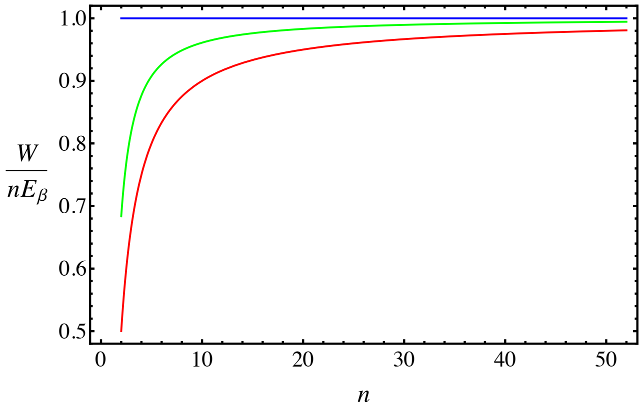

Figure 6.1.: Extractable work from entangled (blue), separable (red), and entangled but having the same entropy as the separable (green) states in units of the initial total energy of the system. Specifically, we take the states (6.10), (6.11), and with $\tau_{\beta'}$ from (6.14) for $d = 2$, $\beta E_1 = 1$. As n increases, classical states become able to store essentially the same amount of work as quantum ones.

In view of these considerations, it is important to understand how one can store work in correlations when the entropy of the state is fixed. On the one hand, having states whose global entropy scales with the number of subsystems seems more realistic. On the other hand, this allows a more fair comparison between entangled and separable states. In this section we will show that quantum coherences and entanglement enhance the work storage capacity even if the entropy of the global state is fixed. This implies that the entropy gap between separable and entangled states mentioned above is not the only reason making classical states generically worse. However, as in the case of non-restricted entropy, the gain provided by entangled states or energy coherences vanishes in the thermodynamic limit.

Stated otherwise, the question is whether locally thermal quantum states subject to the constraint $S(\rho) = S$ can store more work than (6.12) when $S = S(\tau_\beta)$. Now, keeping in mind that local thermality fixes the initial energy to be nE_β, finding the extractable work, $W_{\max}(S)$, amounts to minimizing the final energy, $\mathrm{Tr}(H\sigma)$, over all $\sigma = U\rho U^\dagger$ with U being unitary and ρ satisfying the conditions above.

One can readily lower bound $\mathrm{Tr}(H\sigma)$ by relaxing all the constraints except $S(\sigma) = S$. Then, the state with the least energy compatible with a given entropy is the thermal state,

$$\rho_{\text{th}} = \tau_{\beta'}^{\otimes n} \tag{6.13}$$

with $\beta' = \beta'(S)$ being the unique solution of the entropy constraint $S(\tau_{\beta'}) = S/n$. So, $\mathrm{Tr}(H\sigma) \geq \mathrm{Tr}(H\rho_{\text{th}}) = n\,\mathrm{Tr}(h\tau_{\beta'})$. This implies a bound on the extractable work

$$W_{\max}(S) \leq nE_\beta \left(1 - \frac{1}{E_\beta}\mathrm{Tr}\left(\tau_{\beta'} h\right)\right). \tag{6.14}$$

In principle, it is not clear if the previous bound is attainable, as the way we found ρ_{th} does not guarantee it to be unitarily achievable from any of the allowed initial states. Nevertheless, as we show below, for any given S and any number n of qubits here always exists a locally thermal quantum state that can be transformed to ρ_{th} by a suitable unitary operator, i.e. the bound (6.14) is tight.

Before moving to explicit protocols, let us show a direct consequence of the bound (6.14). As the maximal extractable work from separable states, given in equation (6.12), is obtained for $S = S(\tau_\beta)$, one can easily compare it to $W_{\max}(S(\tau_\beta))$. The result is illustrated in Fig. 6.1, showing that $W_{\text{sep}} < W_{\max}(S(\tau_\beta))$. Therefore, even if the entropy is fixed, classical states are generically weaker than entangled quantum states in terms of work storage as the states delivering $W_{\max}(S(\tau_\beta))$ are necessarily entangled.

Now, let us show an explicit protocol that delivers (6.14). Since to reach the bound in (6.14) the system has to necessarily end up in the state (6.13), we, for clarity, construct the backwards unitary, which takes the final state $\tau_{\beta'}^{\otimes n}$ to an initial state ρ which is locally thermal, at any temperature $\beta \leq \beta'$.

We first consider the simplest case of two qubits. In what follows it will be convenient to introduce the local parameter

$$z = \langle 0|\tau_\beta|0\rangle - \langle 1|\tau_\beta|1\rangle, \tag{6.15}$$

i.e. the "bias" of the local (qubit) subsystem in state τ_β. It is a monotonic function of the temperature: $z = \tanh(\beta E/2)$ (from now on, we concentrate on qubits and, therefore, drop the index of E_1). Define also the unitary transformation U_α as

$$U_\alpha = \begin{pmatrix} \cos\alpha & 0 & 0 & \sin\alpha \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ -\sin\alpha & 0 & 0 & \cos\alpha \end{pmatrix} \tag{6.16}$$

That is, U_α acts as a rotation by an angle α in the subspace spanned by $\{|00\rangle, |11\rangle\}$, and as an identity on the rest of the space.

If as an initial state we take $\rho = U_\alpha \tau_{\beta'}^{\otimes 2} U_\alpha^\dagger$, then since U_α only generates coherences in the subspace where both qubits are flipped, it is clear that the reduced state of each qubit is diagonal. A straightforward calculation shows that under the action of U_α, the state $\tau_{\beta'}$ (with bias z') transforms to an initial state ρ with bias $z = \cos(2\alpha)\, z'$. That is, we can achieve any bias z such that $|z| \leq z'$. As such, the local temperature of the initial state, which is simply given by $\beta = \frac{2}{E}\tanh^{-1}(\cos(2\alpha)\, z')$, can take any temperature $\beta \leq \beta'$ by an appropriate choice of α.

6.5.1. Optimal protocol for n qubits

The above protocol can be readily generalised to the case of n qubits. Let us denote by $\mathbf{i} = i_1 \cdots i_n$ an n-bit string, with $|\mathbf{i}| = \sum_k i_k$. The states

$$|\mathbf{i}\rangle = |i_1\rangle \cdots |i_n\rangle \tag{6.17}$$

run over all 2^n energy eigenstates of H. We also introduce $\bar{\mathbf{i}}$—the bit-wise negated string $\mathbf{i}$, i.e.

$$|\bar{\mathbf{i}}\rangle = \sigma_x^{\otimes n}|\mathbf{i}\rangle. \tag{6.18}$$

Now we show that the unitary $U_{\boldsymbol{\alpha}}$, with $\boldsymbol{\alpha} = \alpha \cdots \alpha$, given by

$$\begin{aligned}
U_{\boldsymbol{\alpha}}|\mathbf{i}\rangle &= \cos\alpha|\mathbf{i}\rangle + \sin\alpha|\bar{\mathbf{i}}\rangle, && \langle\mathbf{i}|H_0|\mathbf{i}\rangle < \tfrac{n}{2}\\
U_{\boldsymbol{\alpha}}|\bar{\mathbf{i}}\rangle &= -\sin\alpha|\mathbf{i}\rangle + \cos\alpha|\bar{\mathbf{i}}\rangle, && \langle\mathbf{i}|H_0|\mathbf{i}\rangle < \tfrac{n}{2}\\
U_{\boldsymbol{\alpha}}|\mathbf{i}\rangle &= |\mathbf{i}\rangle, && \langle\mathbf{i}|H_0|\mathbf{i}\rangle = \tfrac{n}{2}
\end{aligned} \tag{6.19}$$

produces a state $\rho = U_\alpha \tau_{\beta'}(H_S)^{\otimes n} U_\alpha^\dagger$ that is locally thermal with local bias z and temperature β given by

$$\begin{aligned}
z &= \cos(2\alpha)\, z'\\
\beta &= \tfrac{2}{E}\tanh^{-1}(\cos(2\alpha)\, z')
\end{aligned} \tag{6.20}$$

where $z' = \langle 0|\tau_{\beta'}|0\rangle - \langle 1|\tau_{\beta'}|1\rangle = \mathrm{Tr}(\sigma_z\tau_{\beta'})$ is the bias of $\tau_{\beta'}$ (where, for the sake of brevity, we now write $\tau_{\beta'}$ in place of $\tau_{\beta'}(H_S)$ since no confusion should arise). To see that this is the case, we note first that ρ is symmetric under permutations, since both the initial state $\tau_{\beta'}(H_S)^{\otimes n}$ and U_α are symmetric. Therefore it suffices to calculate $z_1 = \langle 0|\rho_1|0\rangle - \langle 1|\rho_1|1\rangle$. We note first that this can be re-written as follows

$$z_1 = \mathrm{Tr}\,(\sigma_z\rho_1) = \mathrm{Tr}\,(\sigma_z \otimes \mathbb{1}_{n-1}\rho) = \sum_{i_1\cdots i_n} \langle \mathrm{i}|(-1)^{i_1}\rho|\mathrm{i}\rangle \tag{6.21}$$

Now, it is straightforward to see that

$$\langle \mathrm{i}|\rho|\mathrm{i}\rangle = \langle \mathrm{i}|U_\alpha \tau_{\beta'}^{\otimes n} U_\alpha^\dagger|\mathrm{i}\rangle = \cos^2\alpha \langle \mathrm{i}|\tau_{\beta'}^{\otimes n}|\mathrm{i}\rangle + \sin^2\alpha \langle \bar{\mathrm{i}}|\tau_{\beta'}^{\otimes n}|\bar{\mathrm{i}}\rangle \tag{6.22}$$

holds for all $|\mathrm{i}\rangle$, and futhermore that $\langle i|\tau_{\beta'}|i\rangle = \frac{1}{2}(1+(-1)^i z')$, which follows from the definition of z' as the bias. Put together, this allows one to re-express z_1 as

$$z_1 = \sum_{i_1\cdots i_n} (-1)^{i_1} \left(\frac{\cos^2\alpha}{2^n} \prod_k (1+(-1)^{i_k} z') + \frac{\sin^2\alpha}{2^n} \prod_k (1+(-1)^{i_k}(-z')) \right) \tag{6.23}$$

which, upon interchanging the order of the product and sum becomes

$$\begin{aligned} z_1 = \frac{\cos^2\alpha}{2^n} \prod_{i_1\cdots i_n} \sum_{i_k} (-1)^{i_1} (1+(-1)^{i_k} z') \\ + \frac{\sin^2\alpha}{2^n} \prod_{i_1\cdots i_n} \sum_{i_k} (-1)^{i_1}(1+(-1)^{i_k}(-z')) \end{aligned} \tag{6.24}$$

For $k \neq 1$, $\sum_{i_k} (-1)^{i_1}(1+(-1)^{i_k} z') = 2$, while for $k = 1$, $\sum_{i_k} (-1)^{i_1}(1+(-1)^{i_k} z') = 2z'$, from which we finally obtain

$$z_1 = \cos^2(\alpha) z' + \sin^2(\alpha)(-z') = \cos(2\alpha) z'. \tag{6.25}$$

The extension of this protocol to arbitrary qudit systems, with arbitrary spectrums, is not straightforward. Partial results were obtained in (HPLH⁺15), where the optimal unitary is constructed for large temperatures. The problem was also solved in (HPLH⁺15) for equally spaced Hamiltonians, but solving it in full generality remains an open question.

6.5.2. Presence of entanglement in the optimal state

Notice that the optimal protocol exploits coherence in all two-dimensional subspaces spanned by $|\mathbf{i}\rangle$ and $|\bar{\mathbf{i}}\rangle$. The coherences that are induced are global, and hence one expects that ρ may be entangled. This is certainly the case for the scenario depicted in Figure 6.1. More generally, let us now study the presence of entanglement in the optimal state $\rho = U_\alpha \tau_{\beta'}^{\otimes n} U_\alpha^\dagger$. We can apply the criterion for entanglement detection developed in (HMGH10; HRHBE12) for a certain bipartition $A|\bar{A}$, which yields an independent positivity condition for each pair of coherences $\langle \mathbf{i}|\rho|\bar{\mathbf{i}}\rangle$, $\langle \bar{\mathbf{i}}|\rho|\mathbf{i}\rangle$,

$$|\langle \mathbf{i}|\rho|\bar{\mathbf{i}}\rangle| - \sqrt{\langle \mathbf{i}|\langle \bar{\mathbf{i}}|\Pi_{A|\bar{A}}\rho^{\otimes 2}\Pi_{A|\bar{A}}|\mathbf{i}\rangle|\bar{\mathbf{i}}\rangle} \geq 0 \tag{6.26}$$

where $\Pi_{A|\overline{A}}$ is the permutation operator acting on the two-copy Hilbert space exchanging partition A between the two copies. If condition (6.26) is satisfied, then the state is entangled. Furthermore, because of the simplicity of the form of ρ (in particular it has an X-like shape), this criterion is necessary and sufficient (HRHBE12).

Focusing on $|\mathbf{i}\rangle = |0...0\rangle$, $|\bar{\mathbf{i}}\rangle = |1...1\rangle$ and on the bipartition $(n/2|n/2)$, the condition for non-separability reads:

$$\sin(2\alpha)(1-e^{-\beta'\epsilon n}) - 2e^{-\beta'\epsilon n/2} \geq 0. \tag{6.27}$$

For sufficiently large n, entanglement will be present in the state for any α. Indeed, when $S(\rho) \propto n$, β' is a constant, and so is α. So, for n large enough, the LHS of (6.27) will be $\approx \sin(2\alpha)$ which is larger than 0. In all other cases, i.e. when $S(\rho) \not\propto n$, which means $S(\tau_{\beta'}) = \frac{S(\rho)}{n} \to 0$ (with $n \to \infty$), $e^{-\beta'\epsilon}$ decreases, so $z' = \frac{1-e^{-\beta'\epsilon}}{1+e^{-\beta'\epsilon}}$ increases, so $\cos(2\alpha) = \frac{z}{z'}$ decreases, so $\sin(2\alpha)$ increases. All in all, the LHS of (6.27) increases with n, becoming positive starting from some value of n.

6.5.3. The thermodynamic limit and classicality

Despite the presence of entanglement and coherence in the optimal ρ, in the thermodynamic limit, the bound (6.14) can always be asymptotically reached by (purely classical) diagonal states. To do so we apply the unitary $U_{\boldsymbol{\alpha}}$ with $\boldsymbol{\alpha}$ chosen appropriately. Consider that α_k is non zero (and equal to $\pi/2$) only for $k = np' - \mu$, i.e. between the subspaces with $|\mathbf{i}| = np' - \mu$ and $|\bar{\mathbf{i}}| = n(1-p') + \mu$, where $p' = \langle 1|\tau_{\beta'}|1\rangle = \frac{1}{2}(1-z')$ is the excited state probability in $\tau_{\beta'}$. That is, we consider the unitary V

$$\begin{aligned} V|\mathbf{i}\rangle &= |\bar{\mathbf{i}}\rangle, & |\mathbf{i}| &= np' - \mu \\ V|\bar{\mathbf{i}}\rangle &= -|\mathbf{i}\rangle, & |\mathbf{i}| &= np' - \mu \\ V|\mathbf{i}\rangle &= |\mathbf{i}\rangle, & &\text{otherwise} \end{aligned} \tag{6.28}$$

In which case, denoting by $\ell = np' - \mu$, we see that z_1 is now given by

$$\begin{aligned} z_1 = z' &- \sum_{|\mathbf{i}|=\ell} \left((-1)^{i_1}\langle\mathbf{i}|\tau_{\beta'}|\mathbf{i}\rangle + (-1)^{\overline{i_1}}\langle\bar{\mathbf{i}}|\tau_{\beta'}|\bar{\mathbf{i}}\rangle\right) \\ &+ \sum_{|\mathbf{i}|=\ell} \left((-1)^{i_1}\langle\mathbf{i}|V\tau_{\beta'}V^\dagger|\mathbf{i}\rangle + (-1)^{\overline{i_1}}\langle\bar{\mathbf{i}}|V\tau_{\beta'}V^\dagger|\bar{\mathbf{i}}\rangle\right) \end{aligned} \tag{6.29}$$

Using the definition of V, and the fact that $(-1)^{\overline{i_1}} = -(-1)^{i_1}$, this can be re-expressed as

$$
\begin{aligned}
z_1 &= z' - 2\sum_{|\mathbf{i}|=\ell} \left((-1)^{i_1}\langle \mathbf{i}|\tau_{\beta'}|\mathbf{i}\rangle + (-1)^{\overline{i_1}}\langle \bar{\mathbf{i}}|\tau_{\beta'}|\bar{\mathbf{i}}\rangle\right) \\
&= z' - 2\Bigg((p')^{\ell}(1-p')^{n-\ell}\left(\binom{n-1}{\ell} - \binom{n-1}{\ell-1}\right) \\
&+ (p')^{n-\ell}(1-p')^{\ell}\left(\binom{n-1}{n-\ell} - \binom{n-1}{n-\ell-1}\right)\Bigg) \\
&= z' - -2\left((p')^{\ell}(1-p')^{n-\ell} - (p')^{n-\ell}(1-p')^{\ell}\right)\binom{n}{\ell}\left(\frac{n-2\ell}{n}\right) \qquad (6.30)
\end{aligned}
$$

where to obtain the second line we used the fact that the probability of a state in the subspace with $|\mathbf{i}| = \ell$ is $(p')^{\ell}(1-p')^{n-\ell}$ and then divided the $\binom{n}{\ell}$ states in the subspace into the $\binom{n-1}{\ell}$ for which $i_1 = 0$ and $\binom{n-1}{\ell-1}$ for which $i_1 = 1$ (and analogously for the subspace with $|\bar{\mathbf{i}}| = n - \ell$).

Using now the definition of ℓ, and the following asymptotic expansion

$$
\begin{aligned}
&(p')^{np'-\mu}(1-p')^{n(1-p')+\mu}\binom{n}{np'-\mu} \\
&\qquad = \sqrt{\frac{1}{2\pi np'(1-p')}}e^{-\mu^2/(2p'(1-p')n)} + O\left(\tfrac{1}{n}\right) \qquad (6.31)
\end{aligned}
$$

after some straightforward manipulations we finally arrive at

$$
z = z'\left(1 - \sqrt{\tfrac{1}{2\pi np'(1-p')}}\left(1 - e^{-\beta' E(nz'+2\mu)}\right)\right) + O\left(\tfrac{1}{n}\right) \qquad (6.32)
$$

which demonstrates that we achieve $z = z'\left(1 - O\left(1/\sqrt{n}\right)\right)$ by swapping only the population between two subspaces within the typical subspace. By applying a sequence of unitaries of the form V with for different values of μ (i.e. corresponding to different subspaces) we therefore see that we can change the local bias (and hence local temperature) of the state by increments of order $1/\sqrt{n}$, which can be made arbitrarily small by choosing n sufficiently large. We note however that the above analysis does not hold if p' becomes too small, approximately of the order $1/\sqrt{n}$. This situation is discussed in detail in Appendix B of (PLHH^{+}15a), where the above protocol is applied for states with submacroscopic entropy.

6.6. Extension to other scenarios

Now we show how our techniques can be applied to other relevant scenarios again in the context of optimal work storage in correlations. In particular, we consider systems where (i) all moments of the energy distribution are equal to those of a global thermal state and (ii) one has access to a thermal bath.

6.6.1. Work from energy coherences

Consider states whose diagonal (in the energy eigenbasis) is set to be equal to that of a global thermal state, together with the initial condition of local thermality. More formally, this approach is equivalent to imposing that all moments of the energy distribution are those of the global thermal state: $\mathrm{Tr}(H^k\rho) = \mathrm{Tr}(H^k\tau_\beta^{\otimes n})$, for all k. This contrasts with the previous sections where only the first moment (i.e. the average energy) was fixed by local thermality. Moreover, notice that the entropy of the initial state is here unconstrained.

Focusing again first on the case of n qubits, we consider states which are maximally entangled in every degenerate subspace:

$$\rho_{\mathrm{deg}} = \sum_{k=0}^{n} \binom{n}{k} p^k (1-p)^{n-k} |D_{n,k}\rangle\langle D_{n,k}| \tag{6.33}$$

where $p = e^{-\beta E}/\mathcal{Z}$, and $|D_{n,k}\rangle \propto \sum_{|\mathbf{i}|=k} |\mathbf{i}\rangle$ is the normalized Dicke state of n qubits with k excitations. It is straightforward to verify that the above state satisfies equation (6.5) and has the required diagonal elements.

The passive state associated to (6.33) can be found as follows. Notice that the state (6.33) is a mixture of $n+1$ orthogonal states. Therefore the optimal unitary amounts to rotating each of these states to the $n+1$ lowest energy levels one of which is the ground state with zero energy and the other n have energy E. Therefore the energy of the transformed state is smaller than E, which means that it is possible to extract all the energy contained in the initial state up to a correction of $\mathcal{O}(1)$:

$$W_{\mathrm{deg}} = nE_\beta - \mathcal{O}(1)E. \tag{6.34}$$

A similar result holds for the general case of n qudits (see Appendix A.2). Therefore we conclude that all work can be stored in the coherences.

An interesting question is whether the state ρ_{deg} features entanglement. Intuition suggests that this may be the case, as large coherences are crucial in this scenario. However, using the techniques developed in (ATSL12), we have not been able to witness entanglement for $n \leq 50$. Based on this evidence, it seems that in this case entanglement may not provide an advantage for any number of subsystems.

6.6.2. Access to a bath

Finally, we consider an extended scenario in which the system is no longer isolated and can be put in contact with a bath at the same (local) temperature. Here, we ask what is the maximal work that can be extracted via unitaries acting jointly on the system and the bath. Then it is known that the extractable work is upper bounded by the difference between initial and thermal free energies (recall our considerations from Chapter 4):

$$W \leq F[\rho] - F[\tau_\beta^{\otimes n}], \tag{6.35}$$

where $F[\rho] = \mathrm{Tr}(H\rho) - \beta^{-1}S(\rho)$ and the inequality can be saturated, see Sec. 4.3 for details.

In the present case, the extractable work from any locally thermal state with entropy S is given by

$$W_{\beta,\max}(S) = \beta^{-1}(nS(\tau_\beta) - S), \tag{6.36}$$

where the expression in parentheses is nothing else but a multipartite generalization of the quantum mutual information. This enforces our argument that the origin of the extractable work are the correlations in the state. The bound (6.36) is strictly bigger than (6.14), which is natural, as we consider a larger set of operations. On the other hand, the states (6.10) and (6.11) maximize the right hand side of (6.36), i.e. the free energy content is maximal, for entangled and separable states respectively, and thus our previous considerations also hold in this framework.

For the case of extracting work from energy coherences, one can readily use (6.36) by computing the entropy of (6.33). As ρ_{deg} is a mixture of $n+1$ pure states, its entropy cannot exceed (and, as can easily be shown, actually scales as) $\ln(n+1)$. Therefore, ρ_{deg} allows for storing all work in coherences except for a $\mathcal{O}(\ln n)$ correcting term. We note that this optimal state cannot be expressed as a tensor product of many coherent states, a situation which was considered previously in the literature (BaHO$^+$13; SSP13).

Notice that, when given access to a bath, the extractable work only depends on a single global property, namely the free energy of the state, which here reduces to the generalized mutual information (6.36). Therefore, the strength of the correlations become the only important property, and not whether they are quantum or not. This is in contrast to our previous results in Sec. 6.5. In order to reconcile both results, imagine that a bath at temperature β' is attached to our system. Then, the bound (6.35) (with β substituted by β') will reduce exactly to (6.14). Therefore we see that separable states can saturate (6.14) when a macroscopic object, i.e. a bath, is available. This corroborates our result in Sec. 6.5, namely that in the thermodynamic limit the difference between quantum and classical correlations vanishes.

Our results in this section thus complement a previous works (DRRV11; FWU13; OHHH02; Zur03; JJR12; DL09), which, in different but related contexts, also deal with the problem of work extraction from thermal environments utilizing correlations. These works include a detailed analysis on the extractable work with local/non-local operations (OHHH02; Zur03), from correlated states (JJR12; DL09), from entanglement with feedback control (FWU13), and also for deterministic work extraction (DRRV11). It is also worth mentioning that when the correlations are not present between subsystems but rather between the system and the bath, they become a source of irreversibility (GRE14).

6.7. Fluctuations of work from entangled states

Let us now combine the considerations of this chapter with those of Chapter 5, where the fluctuations of work where studied. We focus on work extraction from the state (6.10), which is the optimal state for work storage and hence has a great importance in this chapter. Furthermore, this state is particularly interesting because it is pure, entangled, and has all the extractable work in form of correlations.

As a preliminary step, let us consider applying the two projective measurement (TPM) scheme to the state (6.10). The first initial projective measurement would dephase the state, which would become (6.11). In this case, the maximal extractable work becomes (6.12). Importantly, we see that the advantage due to entanglement is lost if such an scheme is applied.

Let us now consider the measurement scheme for the fluctuations of work developed in Sec. 5.8 of Chapter 5. We focus on the case of two qubits, with a Hamiltonian

$$H = \epsilon|1\rangle\langle 1|. \tag{6.37}$$

The initial state (6.10) then reads,

$$|\phi\rangle = (\cos\alpha|00\rangle + \sin\alpha|11\rangle) \tag{6.38}$$

where $\cos^2\alpha = 1/(1+e^{-\beta\epsilon})$ and $\sin^2\alpha = e^{-\beta\epsilon}/(1+e^{-\beta\epsilon})$. Note that

$$\alpha \in [0, \pi/4], \tag{6.39}$$

because we assume positive temperature. It is easy to see that the reduced states of $|\phi\rangle$ are indeed thermal at temperature β. The unitary U extracting work from ρ is U_α, which was introduced in (6.16), and is given by

$$U_\alpha = \begin{pmatrix} \cos\alpha & 0 & 0 & \sin\alpha \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ -\sin\alpha & 0 & 0 & \cos\alpha \end{pmatrix}. \tag{6.40}$$

In Sec. 5.8, we gave the general form for an optimal collective measurement on two copies of the state,

$$\begin{aligned} M^{(ij)} &= |i\rangle\langle i| \otimes T^{(ij)} \\ T_\gamma^{(ij)} &= |U_{ji}|^2 \mathbb{I} + \gamma \sum_{l\neq k} U_{jl} U_{jk}^* |k\rangle\langle l| \end{aligned} \tag{6.41}$$

where γ is a factor to ensure the positivity of the operators. Recall also that $M^{(ij)}$ is the POVM operator associated with the energy transition $i \to j$. For the unitary (6.40) with condition (6.39), we find that

$$\gamma = \tan\alpha \tag{6.42}$$

is enough to satisfy the positivity condition. Recall that this parameter quantifies how invasive the measurement is: For $\gamma = 1$, there is no back action of the apparatus (at least regarding average quantities), and for $\gamma = 0$ the back action is maximal. Given the choice (6.42), we obtain the following transition probabilities for $\rho = |\phi\rangle\langle\phi|$ and U_α,

$$\begin{aligned} p^{(00,00)} &= \langle\phi,\phi|M^{(00,00)}|\phi,\phi\rangle = |\langle\phi\,|00\rangle\,|^2 \langle\phi|T^{(00,00)}|\phi\rangle \\ &= \cos^2\alpha(\cos^2\alpha + 2\cos\alpha\sin^3\alpha) \\ p^{(00,11)} &= \cos^2\alpha(\sin^2\alpha - 2\cos\alpha\sin^3\alpha) \\ p^{(11,00)} &= \sin^2\alpha(\sin^2\alpha + 2\cos\alpha\sin^3\alpha) \\ p^{(11,11)} &= \sin^2\alpha(\cos^2\alpha - 2\cos\alpha\sin^3\alpha). \end{aligned} \tag{6.43}$$

and the other transition probabilities are zero. The probability of ending in the ground state, i.e., of extracting maximal work, is given by,

$$\begin{aligned} p_g = p^{(00,00)} + p^{(11,00)} &= \cos^4\alpha + \sin^4\alpha + 2\cos\alpha\sin^3\alpha = \\ &= 1 - 2\sin^2(2\alpha)(1-\tan(\alpha)) \end{aligned} \tag{6.44}$$

for $\alpha \in [0, \pi/4]$. Let us rexpress it as,

$$p_g = 1 - e(\alpha) \tag{6.45}$$

with,

$$e_\alpha = 2\sin^2(2\alpha)(1 - \tan(\alpha)). \tag{6.46}$$

The quantity e_α measures the strength of the back action of the apparatus. It becomes 1 for $\alpha = \pi/4$, in which case $p_g = 1$, and hence maximal work is extracted. For lower α's, our measurements will decrease the amount of average extracted work. Yet, the effect of entanglement is still present, and appears explicitly in the second summands of the $p^{(ii,jj)}$'s.

6.8. Concluding remarks

In this chapter we investigated and compared the work storing capacities of quantum and classical correlations. To eliminate all sources of work except correlations, we considered systems which are locally thermal. The latter condition is both necessary and sufficient to ensure that the system becomes passive once the correlations are removed. This gives a new perspective on the problem of passivity, in particular for the case of composite systems.

We first show that correlations are powerful enough to allow for the extractable work to be equal to all the energy present in the system (see Sec. 6.3). For that to happen, the state of the system must not only be entangled but also pure, which is impossible for locally thermal separable states due to an entropy constraint. Entanglement is also useful when the state of the system is mixed, as in this case we show that separable states can not generically store the maximal work compatible with the entropy of the system and local thermality. Furthermore, we prove that in all cases the quantum advantage, significant for small ensembles, becomes irrelevant in the thermodynamic limit.

Then we have considered extensions of this scenario, a set of correlated yet locally thermal states. In this respect, first we have studied the role of coherences by further restricting the diagonal of the state in the energy eigenbasis to be identical to a thermal state. Interestingly, in this case it turns out that, in the thermodynamic limit, essentially all the energy can be stored in the off-diagonal terms. Secondly, we have discussed the situation when the system is allowed to interact with a thermal bath at the local temperature of the reduced states. Then, work is directly related to the strength of the correlations as measured by (6.36).

Finally, we also discussed the fluctuations of work when the initial state is entangled. Such fluctuations can not be studied by the usual TPM approach, and the methods developed in Chapter 5 become extremely useful. Focusing on the case of two qubits, we computed the transition probabilities of the different energy exchanges, where a new term appears due to the presence of entanglement. The back action of the apparatus has also been discussed.

7. Thermodynamic Cost of Creating Correlations

7.1. Introduction

The main question explored in this Chapter is the following: what is the thermodynamic cost of establishing classical and quantum correlations? This question clearly complements our considerations of Chapter 6, where we studied how much work can be extracted from correlations. In this chapter we will see how this complementary approach naturally brings new questions and considerations.

In order to determine the thermodynamic cost of creating correlations, our basic starting point is a quantum system composed of two (or more) uncorrelated subsystems, all initially in a thermal state at the same temperature. Note that this is a very natural starting point from the point of view of the resource theory of quantum thermodynamics (BaHO$^+$13), where thermal states at the same temperature are taken for free. In order to establish correlations between the subsystems, we allow ourselves to perform any possible unitary operation on the entire system, which may possibly comprise an external bath. Performing such a unitary will in general cost us some energy.

The first set of questions we seek to answer is how the temperature of the initial state limits the ability to create different types of correlations in the system, starting with classical correlations in bipartite and multipartite systems, before moving into bipartite entanglement and then different forms of entanglement in the multipartite case, including the strongest form – genuine multipartite entanglement. In all cases we seek for the maximal temperature allowing for the generation of entanglement, and provide explicit protocols for generating correlations and entanglement at finite temperature.

We then move on to the question of how the available energy limits the correlations, by determining the maximal amount of correlation that can be created given access to a limited amount of energy. Here our focus is primarily on the bipartite setting, where we investigate optimal protocols for generating classical correlations and bipartite entanglement with limited energy. In the last section we discuss the effect of dealing with interacting systems.

The results of this Chapter are original and published in (HPLH$^+$15; BPLF$^+$15; FHPL). In particular the results of Sec. 7.3 and 7.4 are published in (HPLH$^+$15), the results of 7.5 in (BPLF$^+$15), and finally the results of can be found in (FHPL).

7.2. Framework

We consider a system of n initially uncorrelated d-dimensional quantum subsystems. Each subsystem is taken to have the same (arbitrary) local Hamiltonian H, and the same temperature $k_{\mathrm{B}}T = 1/\beta$. Hence the initial state of the system is

$$\rho_i = \tau_\beta^{\otimes n}, \qquad \text{where } \tau_\beta = \frac{e^{-\beta H}}{\mathcal{Z}} \tag{7.1}$$

and $\mathcal{Z} = \mathrm{Tr}\left(e^{-\beta H}\right)$ is the partition function. When discussing qubits we will denote by E the energy of the excited state and

$$p = \frac{1}{1+e^{-\beta E}} \tag{7.2}$$

the ground state probability. Allowing ourselves the use of arbitrary (global) unitaries U acting on the system, we want to characterise (i) what are the limitations imposed by the initial temperature on the available correlations (either classical or quantum) (ii) what is the energy cost W of creating correlations. If the system is thermally isolated, the work cost reads,

$$W = \mathrm{Tr}\left(H_{\mathrm{tot}}(\rho_{\mathrm{f}} - \tau_\beta^{\otimes n})\right), \tag{7.3}$$

where $\rho_{\mathrm{f}} = U\tau_\beta^{\otimes n}U^\dagger$ is the final state and $H_{\mathrm{tot}} = \sum_i H^{(i)}$ is the total Hamiltonian. Later we will also consider the case of having access to an auxiliary thermal bath at the same temperature.

7.3. Limitations arising from the temperature

First we consider the question of how the temperature of the initial state affects the amount of correlation or entanglement that we can be created. In particular, we impose only that the process can be described by a unitary operation (i.e., the system is closed), and make no further constraints, either in terms of the energy cost of the process, or the efficiency of the implementation. As such, the results presented here constitute fundamental limits on the creation of correlation or entanglement which arise solely from the thermal nature of the initial states, and their corresponding temperature.

We first consider the creation of correlations, both in the bipartite and multipartite settings, before moving on to the question of entanglement generation, again in both the bipartite and multipartite settings.

7.3.1. Correlations

Bipartite systems

Let us start by considering the case of a two qudit system, i.e. two d-level systems. As discussed in 2.2, correlations between the two subsystems (which shall be referred to as S_1 and S_2) can naturally be measured using the quantum mutual information $I_{S_1S_2}$,

$$I_{S_1S_2} = S(\rho_{S_1}) + S(\rho_{S_2}) - S(\rho), \tag{7.4}$$

where $\rho_{S_1} = \mathrm{Tr}_{S_2}\rho$ (and $\rho_{S_2} = \mathrm{Tr}_{S_1}\rho$). The goal is then to find the the optimal unitary operation U such that $\rho_{\mathrm{f}} = U\tau_\beta \otimes \tau_\beta U^\dagger$ has the maximal possible mutual information. Note first that initially $I_{S_1S_2} = 0$, as the initial state factorises. Thus, to create correlations, one must find a global unitary that increases the local entropies $S(\rho_{S_i})$ of ρ_{f}, since the total entropy $S(\rho) = 2S(\tau_\beta)$ cannot change. Since for a d-level system the local entropy is upper bounded by $S_{S_i} \leq \log d$, the maximal possible mutual information is upper bounded by

$$I_{S_1S_2} \leq 2[\log d - S(\tau_\beta)]. \tag{7.5}$$

This bound can always be achieved, by making use of the following protocol, which amounts to rotating from the energy eigenbasis to the generalized Bell basis, i.e. to a basis of maximally entangled qudit states (JJR12). In more detail, for all d one can define the unitary operators

$$X \; = \textstyle\sum_m |m + 1 \bmod d\rangle\langle m|, \qquad Z \; = \displaystyle\sum_m \omega^m |m\rangle\langle m|, \tag{7.6}$$

with $\omega = e^{2\pi i/d}$ as generalisations of the (qubit) Pauli operators σ_x and σ_z. The Bell basis $\{|\phi_{ij}\rangle\}_{ij}$ is then given by

$$|\phi_{ij}\rangle = Z^i \otimes X^j |\phi\rangle, \tag{7.7}$$

where $|\phi\rangle = \frac{1}{\sqrt{d}}\sum_i |ii\rangle$. Finally, we consider the operation given by

$$U = \sum_{ij} |\phi_{ij}\rangle\langle ij|. \tag{7.8}$$

Since the initial state is a mixture of energy eigenstates, ρ_{f} is a mixture of Bell states. Finally, since these all have maximally mixed marginals, i.e. $\mathrm{Tr}_{S_k}(|\phi_{ij}\rangle\langle\phi_{ij}|) = \mathbb{I}/d$ the bound (7.5) is achieved. We end by noting that the maximally mixed state $\mathbb{I}/d$ corresponds to the infinite-temperature thermal state τ_0. We shall see later that when the amount of available work to implement the process is limited, the optimal protocol produces thermal marginals, only there at lower temperatures.

Finally, we note that for all finite initial temperatures $\beta \neq 0$ the mutual information that can be created between the two subsystems is non-zero, i.e. one can produce correlations between them at arbitrary finite temperatures.

Multipartite systems

In the multipartite setting one can generalise the notion of mutual information by considering the difference between the sum of local entropies and the total entropy of the system. That is, for a collection of n subsystems $S_1, \ldots, S_n$, the multipartite mutual information is given by,

$$I_{\{S_1 \cdots S_n\}} = \sum_{i=1}^{n} S(\rho_{S_i}) - S(\rho), \tag{7.9}$$

which vanishes only when the total system is a product. Again, since the total entropy of the system is conserved, to maximise this quantity one must maximise the sum of final local entropies after the protocol. The analogous upper bound,

$$I_{\{S_1 \cdots S_n\}} \leq n(\log d - S(\tau_\beta)), \tag{7.10}$$

is seen to hold, and can again be achieved by rotating the energy eigenbasis to a basis of generalised GHZ states. Namely, one can define the basis $\{|\phi^n_{i_1 \cdots i_n}\rangle\}_{i_1 \cdots i_n}$ by

$$|\phi^n_{i_1 \cdots i_n}\rangle = Z^{i_1} \otimes X^{i_2} \otimes \cdots \otimes X^{i_n} |\phi^n\rangle, \tag{7.11}$$

where $|\phi^n\rangle = \frac{1}{\sqrt{d}} \sum_i |i\rangle^{\otimes n}$ and the operation given by

$$U = \sum_{i_i, \ldots, i_n} |\phi_{i_1 \cdots i_n}\rangle\langle i_1 \cdots i_n|. \tag{7.12}$$

Again, since the final state of the system is a mixture of generalised GHZ states, all of which have maximally mixed marginals $\mathrm{Tr}_{\overline{A}_k}(|\phi_{ij}\rangle\langle\phi_{ij}|) = \mathbb{I}/d$ (where $\overline{A}_k$ denotes tracing over all subsystems except A_k) the bound is seen to be saturated. Finally, as long as the initial temperature is not infinite $\beta \neq 0$, then the bound is non-zero, and a finite amount of correlation can be created between all of the subsystems.

7.3.2. Entanglement

Having seen in the previous section that it is possible to create correlations among the subsystems of a general multipartite system starting at arbitrary temperatures in a relatively easy fashion, we now move on to the move interesting question of creating entanglement. We first look at the case of bipartite systems, where there is a single notion of entanglement, before moving on to multipartite systems, where there are a number of inequivalent notions of entanglement that we will study. In all cases we restrict ourselves to the study of qubits.

Bipartite systems

Let us first consider the simplest possible scenario, involving two qubits. Although there is only a single notion of entanglement, one can nevertheless define many inequivalent measures of it. Here for concreteness we focus on the *concurrence* (Woo98), as defined in Sec. 2.2.2. Recall that for pure states, it is the linear entropy of the reduced state of one party,

$$C(\psi) = \sqrt{2(1 - \mathrm{Tr}(\rho_{\mathrm{A}}^2))}, \tag{7.13}$$

where $\rho_{\mathrm{A}} = \mathrm{Tr}_{\mathrm{B}}|\psi\rangle\langle\psi|_{\mathrm{AB}}$, and is extended to mixed states via the convex-roof construction

$$C(\rho) = \inf \sum_i p_i C(\psi_i), \tag{7.14}$$

where the infimum is taken over all pure state decompositions $\rho = \sum_i p_i |\psi_i\rangle\langle\psi_i|$.

Crucially, for our purposes the problem of finding the state of maximal concurrence given only its spectrum was solved in (IH00; VADM01), which is an alternative way of phrasing the problem which we are interested in here. Moreover, it was shown that the optimal protocol not only maximises the concurrence (and therefore the entanglement of formation), but also two other important measures of entanglement, the relative entropy of entanglement, and the negativity.

The protocol of (VADM01) is easiest understood by decomposing it into a product of two unitaries, $U = V_2 V_1$, where V_1 is a CNOT gate

$$V_1 = |00\rangle\langle 00| + |01\rangle\langle 01| + |11\rangle\langle 10| + |01\rangle\langle 11|, \tag{7.15}$$

and V_2 is a rotation in the subspace spanned by $\{|00\rangle, |11\rangle\}$ to maximally entangled states

$$V_2 = |\phi_{00}\rangle\langle 00| + |01\rangle\langle 01| + |10\rangle\langle 10| + |\phi_{10}\rangle\langle 11|. \tag{7.16}$$

Denoting by $\{\lambda_i\}_i$ the eigenvalues of the initial state $\rho_{\rm i}$ arranged in non-increasing order, the concurrence of the final state $\rho_{\rm f} = V_2 V_1 \rho_{\rm i} V_1^\dagger V_2^\dagger$ is given by

$$C = \max(0, \lambda_1 - \lambda_3 - 2\sqrt{\lambda_2 \lambda_4}). \tag{7.17}$$

Applied to the case at hand, with $\rho_{\rm i} = \tau_\beta \otimes \tau_\beta$ we finally obtain

$$C_{\max} = \max(0, 2p^2 - p - 2(1-p)\sqrt{p(1-p)}). \tag{7.18}$$

It follows therefore, that unlike when considering correlations, there is a now a threshold temperature, $k_{\rm B} T_{\max}/E \approx 1.19$ (or equivalently a threshold ground-state population $p_{\min} \approx 0.698$), such that for all $T \geq T_{\max}$ (or $p \leq p_{\min}$) no entanglement can be created between the two qubits, even if arbitrary unitary operations can be applied.

Multipartite systems

We now switch our attention to the multipartite setting. Here we will see that the limiting temperature $T_{\max}$ below which one can create entanglement can be increased when several copies of the system are jointly processed. Essentially, as more copies are available, the global system contains larger energy gaps and thus subspaces with higher purity, which can be more easily entangled. In the following we make this intuition precise by studying the dependence of $T_{\max}$ on the number of copies n. At the same time, we study several classes of entanglement that naturally appear in the multipartite case including its strongest form: genuine multipartite entanglement.

Entanglement in all bipartitions.

To start our discussion, we consider the case of n qubits and a straightforward generalization of the above two-qubit protocol. That is, we consider a rotation in the $|0\rangle^{\otimes n}$, $|1\rangle^{\otimes n}$ subspace, of the form (7.16),

$$U = |\phi^n\rangle\langle 0|^{\otimes n} + |\phi^{n'}\rangle\langle 1|^{\otimes n} + \mathbb{I} - (|0\rangle\langle 0|)^{\otimes n} - (|1\rangle\langle 1|)^{\otimes n} \tag{7.19}$$

where $|\phi^{n'}\rangle = |\phi^n_{10\cdots 0}\rangle$. For a given bipartition $j|n-j$ (i.e. a partition of j qubits vs. $n-j$ qubits), the concurrence in the final state ρ_f can be conveniently lower bounded using the relation (MCC$^+$11)

$$\begin{aligned} C \quad \geq \quad & 2\Big(\left|\langle 0|^{\otimes n} \rho_f |1\rangle^{\otimes n}\right| \\ & - \sqrt{\langle 0|^{\otimes j}\langle 1|^{\otimes (n-j)} \rho_f |0\rangle^{\otimes j}|1\rangle^{\otimes (n-j)}} \sqrt{\langle 1|^{\otimes j}\langle 0|^{\otimes (n-j)} \rho_f |1\rangle^{\otimes j}|0\rangle^{\otimes (n-j)}} \Big) \end{aligned} \tag{7.20}$$

and due to the simple form of ρ_f, these bounds are in fact tight (HRHBE12). Evaluating explicitly, we then obtain

$$C = \lambda_0 - \lambda_n - 2\sqrt{\lambda_j \lambda_{n-j}}, \qquad \lambda_j = \langle 0|^{\otimes n-j} \langle 1|^{\otimes j} \rho_i |0\rangle^{\otimes n-j} |1\rangle^{\otimes j}. \tag{7.21}$$

which is independent of the bipartition, and given by

$$C = p^n - (1-p)^n - 2p^{n/2}(1-p)^{n/2}. \tag{7.22}$$

By demanding $C > 0$, we can characterise the smallest p, and thus the largest T, that allows for entanglement to be created simultaneously across all bipartitions, as a function of n. We find a linear scaling in n for this critical temperature $T_{\mathrm{E}}^{(\text{all bip.})}$,

$$\frac{k_{\mathrm{B}} T_{\mathrm{E}}^{(\text{all bip.})}}{E} \geq \frac{n}{2\ln(1+\sqrt{2})}. \tag{7.23}$$

Hence it follows that entanglement across all bipartitions can always be generated starting from an arbitrary temperature T, by considering a sufficiently large number of qubits n. We note also that if one used instead of concurrence the negativity across a bipartition, a straightforward calculation shows that the same bound is obtained.

Entanglement in a single bipartition.

The above protocol can be improved if the aim is to generate entanglement in a given single bipartition $j|n-j$. As in the two-qubit protocol, the idea is to perform a permutation of the initial diagonal elements before applying the rotation (7.19). From expression (7.21), we see that the optimal permutation is the one where $\lambda_0 = p^n$, $\lambda_n = \lambda_j = p(1-p)^{n-1}$ and $\lambda_{n-j} = (1-p)^n$. In such a case, we a similar analysis to above leads to the limiting temperature, which, for large n is given by

$$\frac{k_{\mathrm{B}} T_{\mathrm{E}}}{E} \gtrsim \frac{n-1/2}{\ln(3)}. \tag{7.24}$$

Hence the threshold temperature for the creation of bipartite entanglement using this protocol is also linear in n (for high temperatures), but improves upon the above protocol in the constant. Thus for fixed n, one can generate entanglement across a single bipartition for slightly higher temperatures with this protocol.

Genuine multipartite entanglement I

Genuine multipartite entanglement (GME) is the strongest form of entanglement in multipartite systems. A state ρ is GME iff ρ only admits decompositions of the form

$$\rho = \sum_i p_i |\phi_i\rangle\langle\phi_i| \tag{7.25}$$

where at least one $|\phi_i\rangle$ is entangled in every possible bipartition. It follows that a necessary but not sufficient condition for GME is that ρ itself is entangled across every bipartition. This suggests that the previously considered protocol for generating entanglement in all bipartitions is a natural candidate to gain a first insight on the maximal temperature for GME creation.

After applying the unitary (7.19), the state ρ_f is essentially a GHZ-state mixed with (diagonal) noise. For such a simple form, the techniques of Ref. (MCC$^+$11; HPLdV13) give us the necessary and sufficient conditions for the creation of GME (HRHBE12), namely

$$\rho_f \text{ is GME} \iff p^n - (1-p)^n - 2(2^{n-1}-1)p^{n/2}(1-p)^{n/2} \geq 0 \tag{7.26}$$

This condition leads to a lower bound on the threshold temperature for creating GME, T_{GME}, which turns out to be asymptotically independent of n, and given by

$$\frac{k_{\text{B}} T_{\text{GME}}^{(\text{GHZ})}}{E} \simeq \frac{1}{2\ln(2)}. \tag{7.27}$$

where we added the suffix GHZ because the target entangled state of this protocol is a GHZ state. Moreover, as we show in the Appendix A.3, this result holds for all states whose density matrix features only diagonal and anti-diagonal elements, also known as X-states.

Genuine multipartite entanglement II

Recall that there are many inequivalent types of multipartite entangled states and GHZ states only constitute one prominent class. In fact it is much more favorable to use protocols that target another type of entangled states, namely Dicke states (Dic54). An n-qubit Dicke state with k excitations is defined as:

$$|D_k^n\rangle = \frac{1}{\sqrt{\binom{n}{k}]}} \sum_j P_j\{|1\rangle^{\otimes k}|0\rangle^{\otimes n-k}\} \tag{7.28}$$

where $\sum_j P_j\{\}$ is a sum over all possible permutations. Besides being relevant for the theory of light-matter interaction, Dicke states are useful for various quantum information tasks (CGP$^+$12), have been detected experimentally (WKK$^+$09) and have shown to exhibit genuine multipartite entanglement (Dua11; LPV$^+$14).

By constructing a protocol that uses the state (7.28) as the target entangled state, we obtain that the threshold temperature for generating GME is given by

$$\frac{k_{\mathrm{B}}T_{\mathrm{GME}}}{E} \geq \frac{n}{(k+1)\ln n} + \mathcal{O}\left[\frac{n}{(\ln n)^2}\right]. \tag{7.29}$$

The scaling is almost linear with n, which allows now for the creation of GME for an arbitrarily high temperature $T < \infty$, by considering a sufficient number of qubits n. Note that this result is quite counter-intuitive, as the complexity of the task we consider, entangling all qubits, increases with n. Furthermore, it in stark contrast with the results obtained above for the GHZ class, and thus indicates that different types of entanglement behave in a very different manner.

Let us now sketch the idea of the protocol for creating Dicke type entanglement; all details are in Appendix A.4. As in the previous cases, the protocol consists of two steps: a permutation of the diagonal elements followed by a rotation to maximally entangled states (in this case to Dicke states). The permutation first moves the largest eigenvalue, p^n, plus the small eigenvalues, $p^k(1-p)^{n-k}$, into the degenerate subspace of energy kE, thus purifying the subspace. It also moves other small eigenvalues[1] into the subspaces of $k-1$ and $k+1$ excitations, as this is favorable for the considered entanglement witness (HES$^+$11). Now, in the degenerate subspace of k excitations, the state with the biggest population p^n is rotated to the Dicke state. In order for the transformation to be unitary, the rest of the energy eigenvectors of the subspace are rotated to the set of orthonormal states

$$|d^n_{k,l}\rangle = \frac{1}{N_k}\sum_j e^{i\frac{2\pi l j}{N_k}} P_j\{|1\rangle^{\otimes k}|0\rangle^{\otimes n-k}\}, \qquad N_k = \sqrt{\binom{n}{k}}. \tag{7.30}$$

with $i = \{1, ..., N_k - 1\}$. This concludes the protocol leading to (7.29) (see Appendix A.4 for detailed computations).

The fact that the creation of Dicke type GME is so much more favorable can be understood intuitively by recalling that Dicke states are in general much more robust to noise compared to GHZ states (HES$^+$11). Notice also from (7.29) that it is most favorable to create entanglement in the first excited subspace, where the Dicke state becomes the well-known W state.

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[1] i.e., eigenvalues with population $p^{n-m}(1-p)^m$ with $m/n \to 0$ in the asymptotic limit.

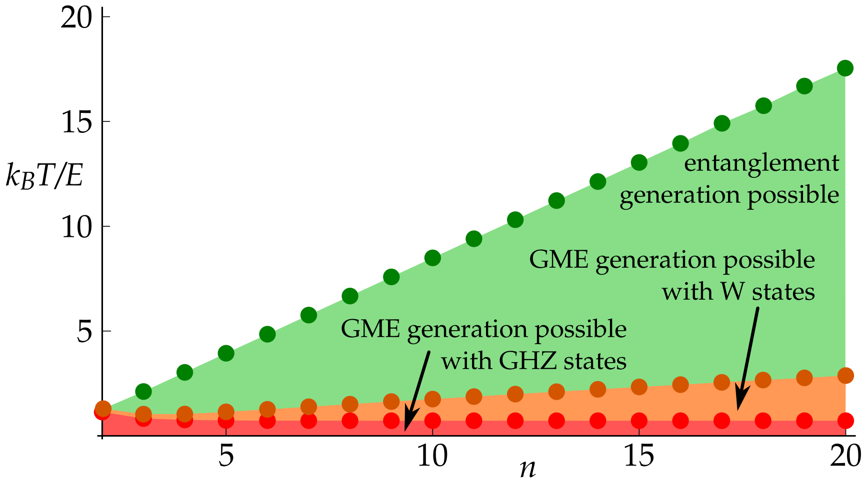

Figure 7.1.: Regions where entanglement creation (green area) and GME creation (orange area) are possible by our explicit protocols. The upper (green) points represent the best protocol for entanglement creation in a qubit/qudit bipartition, and also an upper bound for creation of GME. The scaling for each region are given in the main text.

Upper bounds and discussion

So far, we have investigated explicit protocols, which allowed us to place lower bounds on the threshold temperature that still allows for the creation of entanglement. To study the limitations imposed by a thermal background it is essential to also find upper bounds on the maximal temperature. For that purpose, a first approach is to use results on the geometry of quantum states. In particular, it is known that the maximally mixed state is always surrounded by a ball of finite size that contains only separable states, and it is possible to place lower bounds on the radius of such a ball (GB02; GB03). By applying these results we obtain an upper bound that scales exponentially with n. Therefore, there is an exponential gap between lower and upper bounds, thus making this approach essentially useless for large n.

The results from (GB02; GB03) are useful for any state, as long as it is sufficiently close to the identity, whereas here we are concerned with a very particular form of states, namely those states with a thermal spectrum. This information can be used to obtain better upper bounds. Indeed, the following theorem was proven in ref. (Joh13): let $\rho \in \mathcal{H}_2 \otimes \mathcal{H}_d$ have eigenvalues $\lambda_1 \geq$

$\lambda_2 \geq ... \geq \lambda_{2d}$, then

$$U\rho U^\dagger \text{ is separable } \forall U \iff \lambda_1 - \lambda_{2n-1} - 2\sqrt{\lambda_{2n-2}\lambda_{2n}} \leq 0. \tag{7.31}$$

By taking $d = 2^{n-1}$, this criterion applies to any qubit/qudit bipartition of the n-qubit thermal system we considered. Furthermore, notice that this condition amounts to calculating the concurrence in a specific 4×4 subspace, which happens to be exactly the purest one we used in the protocol leading to (7.24). Hence that protocol is optimal for generating entanglement in any qubit/qudit bipartition. While the possibility to obtain a better T_{E} in a qudit/qudit bipartition remains open, this criterion does yield upper bounds for $T_{\mathrm{E}}^{(\text{all bip.})}$ and T_{GME} [2], obtaining

$$\begin{aligned} \frac{k_{\mathrm{B}} T_{\mathrm{E}}^{(\text{all bip.})}}{E} &\leq \frac{n-1}{\ln 3}, \\ \frac{k_{\mathrm{B}} T_{\mathrm{GME}}}{E} &\leq \frac{n-1}{\ln 3} \end{aligned} \tag{7.32}$$

Therefore we obtain upper bounds on (7.23) and (7.29) that also scale linearly with n, showing that this scaling between the maximal temperature and the number of qubits is a fundamental property, and that our protocols perform close to optimal for entanglement and GME generation at high temperatures. The results are summarized in fig. 7.3.

The problem of the attainable entanglement in the unitary orbit of mixed states has been considered in the context of nuclear magnetic resonance (see (YBC05) and references therein). The best protocol in ref. (YBC05) obtains precisely the scaling (7.23), improving on protocols based on algorithmic cooling and effective pure states (DC00). Our result (7.24) provides a tighter bound on the minimal temperature required for entanglement generation, and the upper bound derived from ref. (Joh13) gives evidence that it is tight.[3] We also studied the minimal temperature for GME, finding a surprising positive scaling with the number of qubits. Our results thus provide the first bounds on the number of qubits required to generate entanglement and GME at finite temperature, while showing that in the asymptotic limit generation of entanglement and GME is possible at any temperature.

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[2] recall that the presence of entanglement in every bipartition is a necessary condition for GME.

[3] Recall that this upper bound only applies for qubit/qudit bipartitions

7.4. Energy cost in thermally isolated systems

We can associate to every operation U a work cost W, given in (7.3), which corresponds to the external energy input. Regardless of the operation U, the invested work is always positive because the initial state is in thermal equilibrium, i.e., $W \geq 0 \; \forall U$. This naturally raises the following question: what is the minimal work cost of correlating thermal state? or, equivalently, what is the maximal amount of attainable correlations when the energy at our disposal, ΔE, is limited? In this section we address these question, both for total correlations and entanglement, in the unitary orbit of thermal states (i.e., optimising over all global unitaries U).

The results of this section and the next one are original and based upon (HPLH$^+$15).

7.4.1. Correlations

In analogy with the previous section, let us start by considering the case of a two qudit system, i.e. two d-level systems. The goal is now to maximize $I_{S_1 S_2}$, as defined in (7.4), over all global unitaries constrained by $W \leq \Delta E$.

Note first that initially $I_{S_1 S_2} = 0$, as the initial state factorises. Now, to create correlations, we must apply a global unitary that will increase the local entropies S_{S_i} of ρ_f, since the total entropy $S(\rho) = 2S(\tau_\beta)$ will clearly not change. Recalling that the thermal state maximises the entropy of a system with fixed average energy, we find that

$$I_{\Delta E} \leq 2 \left[S(\tau_{\beta'}) - S(\tau_\beta) \right], \tag{7.33}$$

where β' is chosen such that $\Delta E = \mathrm{Tr}[H_{\mathrm{tot}}(\tau_{\beta'}^{\otimes 2} - \tau_{\beta}^{\otimes 2})]$. Hence in order to obtain correlations at minimal energy cost, one should look for a protocol such that the local states of ρ_f are thermal states at equal temperature. That is, the optimal unitary U^* satisfies

$$\mathrm{Tr}_{S_1}(U^* \rho_i U^{*\dagger}) = \mathrm{Tr}_{S_2}(U^* \rho_i U^{*\dagger}) = \tau_{\beta'}. \tag{7.34}$$

This unitary effectively heats up the system locally, while the global system preserves its entropy. Finally, notice that expression (7.33) recovers the case of maximal correlations, (7.33), in the limit $\beta' \to 0$, with a corresponding work cost,

$$W = 2 \left(\frac{1}{d} \mathrm{Tr} H - \frac{1}{\mathcal{Z}} \mathrm{Tr} H e^{-\beta H} \right). \tag{7.35}$$

These results are easily extendible to the multipartite case. The generalized mutual information (7.9) is maximized (for a given energy cost) by those unitaries that satisfy (7.34) for every local state.

In the case of qubit systems, the optimal unitary is precisely the inverse unitary constructed in Sec. 6.5 of Chapter 6. Indeed, one easily sees that by running the optimal protocol of Sec. 6.5 backwards, one obtains the optimal protocol for the problem considered here. Therefore, the starting point of Chapter 6 is the optimal ending point here; and vice versa. That is, the two processes become the reverse of each other *only* when they are both optimal. This situation is in fact common in thermodynamics. For example, a heat engine working at Carnot efficiency can be seen as an optimal refrigerator running backwards. Our protocols thus exemplify this relation for the complementary problems of creating correlations from work, and extracting work from correlations.

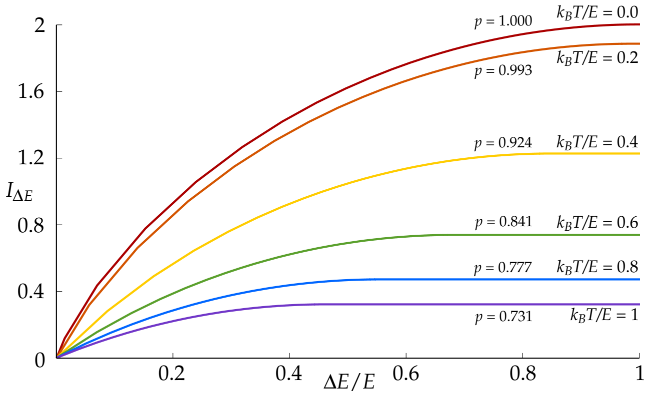

Figure 7.2.: Mutual information vs. available energy, for various values of $k_\mathrm{B}T/E$.

7.4.2. Entanglement

Bipartite systems

Next we derive the minimal work cost of creating entanglement for the simplest case of two qubits. Consider first the case $T = 0$, i.e. $\tau = |0\rangle\langle 0|$. If the state is pure, entanglement can be measured by the entropy of entanglement, which is simply given by the local entropy of the state. The problem at hand is thus equivalent to the maximization of the mutual information, so the same reasoning can be used here[4]. In particular, the optimal unitary, U^* in (7.34), corresponds to the inverse of U_α, given in (6.16). From this we find the relation,

$$C = \sqrt{\frac{\Delta E}{E}\left(2 - \frac{\Delta E}{E}\right)}. \tag{7.36}$$

Moving to non-zero temperature, finding the optimal unitary is no longer straightforward. Nevertheless the problem can be attacked from two directions. First, we maximize C numerically, with respect to all possible unitaries, for a given cost W. Second, we use an ansatz protocol, inspired by the optimal unitaries to achieve $C_{\max}$ in (7.17). These unitaries have the form of first rotating in the subspace of $|10\rangle$ and $|11\rangle$, followed by rotating in the subspace of $|00\rangle$ and $|11\rangle$. Our ansatz is to optimise over such unitaries, now a much simpler optimisation over the two unknown angles (one for each rotation). The results are presented in Fig. 7.3, where the solid line shows the result of the full optimisation and the dashed line shows the results of the ansatz. We see that when there is no restriction on the amount of available energy W, then our ansatz protocol performs optimally. However, this is not the case when W is limited. Note that the amount of energy required to reach $C_{\max}$ is decreasing as T increases, shown in inset (a), where we also see that for low temperatures ($k_B T/E \lesssim 0.1$), we can generate essentially one Bell state of two qubits, i.e. $C_{\max} \simeq 1$. Moreover, for any $T > 0$, there is a minimal amount of energy required for generating entanglement, shown in inset (b). This is because some energy is always needed to leave the set of separable states.

Multipartite systems

Quantification and characterization of multipartite entanglement is still a highly active field of research (see e.g. Ref. (ES14)). The main challenge is a consistent quantification of multipartite entanglement in operational terms, but, as we discussed in the Sec. 2.2.2, this task may not be as easy as in bipartite systems. Here we circumvent this issue by studying a measure independent question: what is the energy cost of transforming a thermal state into an entangled one, either GME or entangled in all bipartitions?

The work cost associated to the unitary (7.19) is easily computed to be

$$W = \frac{nE(1 - e^{-\beta E n})}{2(1 + e^{-\beta E})^n}. \tag{7.37}$$

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[4] Note that the concurrence and the entropy of entanglement are isomorphic for two qubits

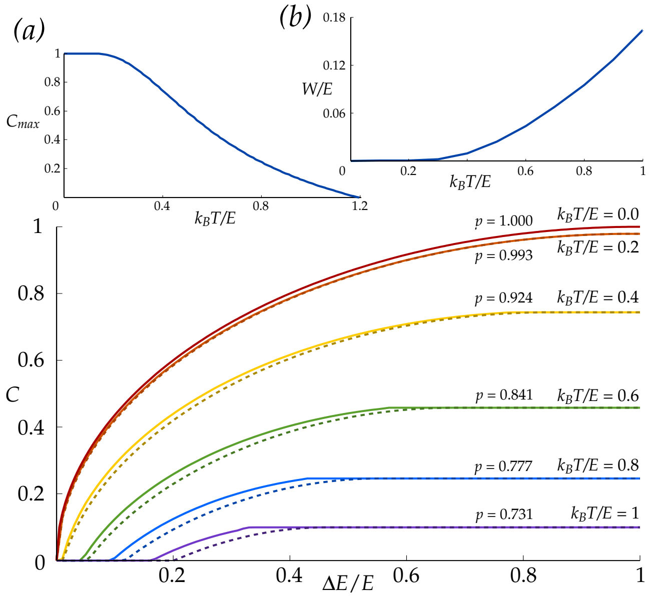

Figure 7.3.: Main: Concurrence vs. available energy, for various values of $k_\mathrm{B}T/E$. Solid lines show the optimal protocol, found numerically by optimising over the unitary group. The dashed lines show the performance of the simpler protocol, described in the main text, which is seen to perform well, especially for smaller temperatures. Moreover, if the available energy is not limited, our ansatz is optimal. Inset (a) shows the behaviour of the maximal concurrence C_max as a function of $k_\mathrm{B}T/E$, while inset (b) shows the energy needed to leave the separable set, as a function of $k_\mathrm{B}T/E$.

By inserting $T^{\text{all bip.}}$ in (7.37), one obtains that the cost to leave the separable set (for this particular protocol) is exactly

$$W^{\text{sep.}} = nE\frac{1+\sqrt{2}}{\left(\left(1+\sqrt{2}\right)^{2/n}+1\right)^{n}} \tag{7.38}$$

which is exponentially small in n. This shows that having more copies not only opens the possibility to generate entanglement at a higher temperature, but also reduces the energy cost of leaving the separable set. An exponential decrease of the work cost with n is also found for the other protocols for GME generation in the multipartite setting (see Appendix A.4). The reason behind this behavior is that the considered protocols only act on particular subspaces, whose population becomes negligible in the limit of large n. This also implies that the amount of generated entanglement decreases with the number of copies. Interestingly, in the multipartite setting, even a small amount of entanglement might be enough to obtain a substantial quantum advantage. In particular, in the field of quantum computation, for a computational speed up (in pure states) entanglement is required across every bipartition (Vid03), but the actual amount can be polynomially small in the system's size (VdN13). [5]

7.5. Energy cost in the presence of an external bath

We now move to the scenario where an external bath B is available. The results presented in this section are original and based upon (BPLF^{+}15). For simplicity of the discussion, we focus on the creation of correlations, as quantified by the mutual information, in bipartite systems. Hence, the relevant magnitude is simply

$$I_{S_1S_2} = S(\rho_{S_1}) + S(\rho_{S_2}) - S(\rho_S) \tag{7.39}$$

where we added the subindex S to differentiate the system of interest of the bath B. That is, in this case we have a system S made up of two subsystems S_1, S_2, in contact with a Gibbs state B. Here our considerations of Chapter 4 become useful. In particular, we use expression 4.10,

$$W = \Delta F_S + \Delta F_B + TI_{SB}, \tag{7.40}$$

where ΔF_S (ΔF_B) is the change of free energy of S (B). We now split ΔF_S into the free energy differences of its subsystems, and their correlations as

$$\Delta F_S = \Delta F_{S_1} + \Delta F_{S_2} + TI_{S_1S_2}, \tag{7.41}$$

Finally, using the identity, $\Delta F = TS\left(\rho \| \tau(\beta)\right)$ which holds for thermal states τ, we have,

$$\beta W = S(\rho_{S_1} \| \tau_{S_1}) + S(\rho_{S_2} \| \tau_{S_2}) + S(\rho_B \| \tau_B) + I_{S_1S_2} + I_{SB}, \tag{7.42}$$

where ρ_{S_1}, ρ_{S_2}, and ρ_B denote the final reduced states for the subsystems, S_1 and S_2, and the bath B, respectively. In other words, work can be invested to shift the thermal marginals away from equilibrium or to create correlations.

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[5] This translates to density matrices through the convex roof: If every possible decomposition requires at least one element that is entangled across all partitions we can conclude that the classical simulation will be hard and the dynamics of the system non-trivial (while it is not at all clear whether this is necessary it is at least sufficient).

Since all quantities on the right-hand side of Eq. (7.42) are non-negative, it follows,

$$I_{S_1S_2} \leq \beta W. \tag{7.43}$$

This gives an upper bound on the amount of correlations that can be created given some available work W and an external bath at temperature T.

Remarkably, it is possible to saturate this bound using a simple protocol, which can be divided into two steps (see also Fig. 7.5):

1. **C**ooling: First, the temperature of S is lowered from T to $T_{\mathrm{I}} \leq T$, reducing the global entropy of the system. The (minimal) energy cost for this thermalization process is the change of free energy, which, as discussed in Chapter 4, can be obtained if a sufficiently large bath is available. In this case, $W_{\mathrm{I}} = \Delta F_S$, and,

   $$W_{\mathrm{I}} = F\left(\tau_S(\beta_{\mathrm{I}})\right) - F\left(\tau_S(\beta)\right), \tag{7.44}$$

   where $\beta_{\mathrm{I}} = 1/T_{\mathrm{I}}$.

2. **C**orrelating: In the second step, the system is isolated from the bath and it is correlated via a unitary operation U_{corr}. Following our previous considerations, the unitary is chosen such that S_1 and S_2 are locally thermal at temperature $T_{\mathrm{II}} = 1/\beta_{\mathrm{II}} \geq T_{\mathrm{I}}$,

   $$\mathrm{Tr}_{S_1(S_2)}\left(U_{\mathrm{corr}}\tau_S(\beta_{\mathrm{I}})U_{\mathrm{corr}}^{\dagger}\right) = \tau_{S_2(S_1)}(\beta_{\mathrm{II}}). \tag{7.45}$$

   Recall that this choice ensures that the systems are correlated at minimal energy cost W_{II}.

There is thus a tradeoff between the amount of work W_{I}, invested to cool down the system, which allows one to potentially obtain larger correlations, and the work W_{II}, invested to actually correlate it. It is straightforward to obtain that both contributions add up to

$$W = W_{\mathrm{I}} + W_{\mathrm{II}} = TI_{S_1S_2} + TS\left(\tau_S(\beta_{\mathrm{II}})\|\tau_S(\beta)\right). \tag{7.46}$$

Therefore, optimality is achieved when the local temperature of the final state marginals is identical to the initial temperature, $T_{\mathrm{II}} = T$, such that $W = TI_{S_1S_2}$. However, this is not always achievable. Setting $\beta_{\mathrm{II}} = \beta$ may require W_{I} to become larger than the energy that is necessary to cool down to the ground state. This leads to a surplus of energy for the correlation step. In such a

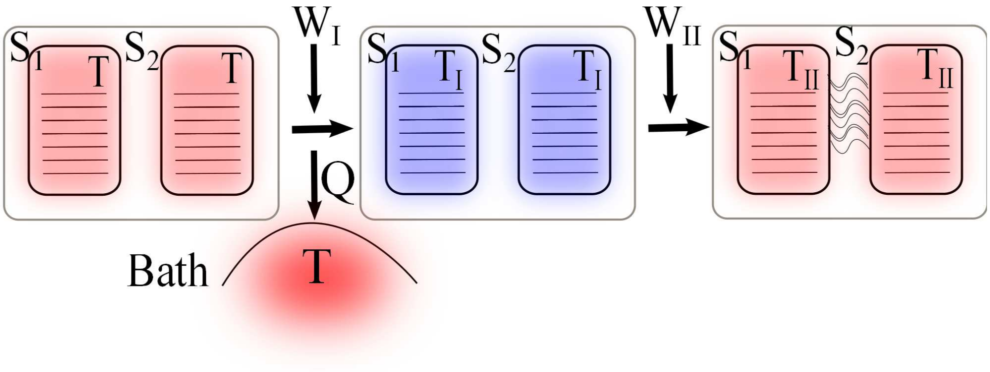

Figure 7.4.: Illustration of the protocol: In the first step the system is cooled down by a controlled interaction with the bath, and the heat Q is transferred to the bath. The associated work cost is W_{I}. In the second step, the system is isolated from the bath before it is correlated though a unitary operation, which effectively heats up the subsystems. The energy cost of the second step is W_{II}.

case, T_{II} is larger than the initial temperature T. The transition to this regime occurs when,

$$W = \tilde{W} = \tilde{W}_{\mathrm{I}} + \tilde{W}_{\mathrm{II}} = T\,S\left(\tau_S(\beta)\right), \tag{7.47}$$

where $\tilde{W}_{\mathrm{I}} = -F\left(\tau_S(\beta)\right)$ corresponds to the energy necessary to cool down to the ground state and $\tilde{W}_{\mathrm{II}} = E\left(\tau_S(\beta)\right)$ is the work necessary to correlate the systems such that $\beta_{\mathrm{II}} = \beta$. After some rearranging, one obtains

$$I_{S_1 S_2} \leq \begin{cases} \beta W & \text{if } \beta W \leq S\left(\tau_S(\beta)\right), \\ S(\tau_S(\beta_{\mathrm{II}})) & \text{if } \beta W > S\left(\tau_S(\beta)\right), \end{cases} \tag{7.48}$$

where β_{II} is given by the implicit relation

$$E\left(\tau_S(\beta_{\mathrm{II}})\right) = W + F\left(\tau_S(\beta)\right). \tag{7.49}$$

There are thus two fundamentally different regimes for the generation of mutual information. We discuss this in detail in the next section for a system of two bosonic modes.

Before moving to a particular physical system, it is worth mentioning that our protocol is extendible to nonequilibrium initial states. One then needs to first extract the work content of the state, which leaves it in a thermal state at the temperature of the bath. Our protocol can then be readily applied using the extracted work in addition to any externally supplied energy to correlate the system.

7.5.1. A case study: Two bosonic modes

Let us examine more closely the scaling of the generated correlations with the input energy for a system of two bosonic modes, or equivalently two systems with an equally spaced infinite spectra. We take two systems with identical internal Hamiltonian, $H = H_{S_1} + H_{S_2}$

$$H_{S_i} = \sum_k \left(\frac{1}{2} + k\right) \omega |k\rangle\langle k|, \tag{7.50}$$

where we implicitly assumed $\hbar = 1$. The initial state is thermal, $\tau_S = \tau_\beta^{\otimes 2}$, with $\tau = \sum_k p_k |k\rangle\langle k|$, and $p_k = \frac{e^{-k\beta\omega}}{1-e^{-\beta\omega}}$. Being thermal states of an the quantum harmonic oscillator, the total energy and entropy of the two mode system can be computed yielding,

$$E(\tau_S(\beta)) = 2\mathrm{Tr}(H\tau) = \omega \coth \frac{\beta\omega}{2} \tag{7.51}$$

$$S(\tau_S(\beta)) = -2\mathrm{Tr}(\tau \ln \tau) = 2h\left(\coth \frac{\beta\omega}{2}\right) \tag{7.52}$$

with,

$$h(x) = \frac{1+x}{2} \ln \frac{1+x}{2} - \frac{x-1}{2} \ln \frac{x-1}{2}. \tag{7.53}$$

By using expressions (7.51) and (7.52), one can easily compute the minimal work cost of correlations obtained through the optimal protocol described in the last section. The results are shown in Fig. 7.5.1. The figure clearly illustrate two regimes, a linear and a sublinar one, in perfect agreement with (7.48).

In order to gain a better understanding on the sublinear region, let us now consider the regime where the supplied energy W is much larger than $S\left(\tau_S(\beta)\right)/\beta$. In this limit, we can expand $h(x)$ over $1/x \to 0$ and use that $S = 2h(E/\omega)$ to obtain

$$S(\tau_S(\beta_{II})) = 2\ln\left(\frac{e}{\omega} E((\tau_S(\beta_{II}))\right) + \mathcal{O}\left(\frac{\omega^2}{E((\tau_S(\beta_{II}))^2}\right). \tag{7.54}$$

or equivalently,

$$I_{max} = 2\ln\left(\frac{e}{\omega}(W + F(\tau_S(\beta_{II}))\right) + \mathcal{O}\left(\frac{\omega^2}{W^2}\right). \tag{7.55}$$

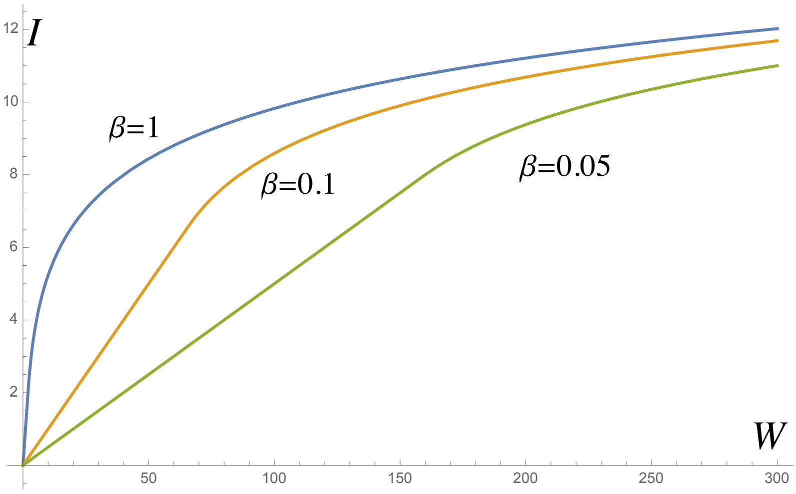

Figure 7.5.: Mutual information as a function of the invested work for a two bosonic mode.In the figure we can appreciate the two regimes, linear and sub-linear, as expected from (7.48)

which shows that, when the work input is big, the generation of correlations increases logarithmically with it, $I_{\text{max}} \propto \ln W$. This small increasing is in sharp contrast with the linear increase at small energies (see again Fig. 7.5.1).

7.6. Energy cost of correlations in the presence of interactions

Finally, we study how the presence of interactions modifies the previous bounds obtained. These results presented here are original and based on (FHPL). In particular, we are interested in understanding whether the relation $W \geq T I_{S_1 S_2}$ can be violated, i.e., we can reduce the minimal work cost of correlations by making use of the energy contained in the interacting term of the Hamiltonian. We take for the system a Hamiltonian of the form,

$$H_S = H_{S_1} + H_{S_2} + H_I. \tag{7.56}$$

It is important to note that in this case, the initial state of S,

$$\tau = \frac{e^{-\beta(H_{S_1}+H_{S_2}+H_I)}}{\mathcal{Z}} \tag{7.57}$$

is already correlated. Hence in order for a fair comparison with the non-interacting case, we focus our attention in the gain of correlations, $\Delta I_{S_1 S_2}$.

As discussed above, the work cost of transforming $\tau(\beta)$ to a final state ρ satisfies, $W(\tau \to \rho) \geq \Delta F_S = F(\rho) - F(\tau)$. After some straightforward manipulations we can express ΔF_S with the Hamiltonian (7.56) as,

$$\Delta F_S = T\Delta I_{S_1 S_2} + \mathrm{Tr}\left(H_I[\rho - \tau]\right) + \Delta\tilde{F}_{S_1} + \Delta\tilde{F}_{S_2}, \tag{7.58}$$

where the quantities $\tilde{F}_{S_1(S_2)}$ correspond to nonequilibrium free energies with respect to the local Hamiltonians, i.e.,

$$\tilde{F}_{S_i}(\rho) = \mathrm{Tr}\left(H_{S_i}\rho\right) - TS(\rho_{S_i}) \tag{7.59}$$

with $\rho_{S_1(S_2)} = \mathrm{Tr}_{S_2(S_1)}\,\rho$.

In order to develop strategies that can outperform the bound (7.43), it is convenient to express the density operators of a bipartite qudit system according to the generalized Bloch-Fano decomposition (Fan83; AK08),

$$\rho = \frac{1}{d_1 d_2}\left(\mathbb{I}_S + \sum_{m=1}^{d_1^2-1} a_m \sigma_m^{S_1} \otimes \mathbb{I}_{S_2} + \sum_{n=1}^{d_2^2-1} b_n \mathbb{I}_{S_1} \otimes \sigma_n^{S_2} + \sum_{m=1}^{d_1^2-1}\sum_{n=1}^{d_2^2-1} c_{mn}\,\sigma_m^{S_1} \otimes \sigma_n^{S_2}\right) \tag{7.60}$$

where d_1 and d_2 are the dimensions of the local systms, the Hermitean operators $\sigma_m^{S_i}$ satisfy $\mathrm{Tr}(\sigma_m^{S_i}\sigma_n^{S_i}) = 2\delta_{mn}$ and $\mathrm{Tr}(\sigma_m^{S_i}) = 0$, and the real coefficients a_m, b_n, and t_{mn} are subject to constraints arising from the positivity of ρ. The reduced states are then immediately obtained as

$$\rho_{S_1} = \frac{1}{d_1}\left(\mathbb{I}_{S_1} + \sum_{m=1}^{d_1^2-1} a_m\,\sigma_m^{S_1}\right), \tag{7.61a}$$

$$\rho_{S_2} = \frac{1}{d_2}\left(\mathbb{I}_{S_2} + \sum_{n=1}^{d_2^2-1} b_n\,\sigma_n^{S_2}\right). \tag{7.61b}$$

The Hermitean interaction Hamiltonian can similarly be written as

$$H_I = \sum_{m=1}^{d_1^2-1}\sum_{n=1}^{d_2^2-1} \epsilon_{mn}\,\sigma_m^{S_1} \otimes \sigma_n^{S_2}, \tag{7.62}$$

with real coefficients ϵ_{mn}. Any terms of the form $\mathbb{I}_{S_1} \otimes \sigma_m^{S_2}$ and $\sigma_m^{S_1} \otimes \mathbb{I}_{S_2}$ that may appear in such a decomposition of H_I can be absorbed into the local Hamiltonians H_{S_i}.

Returning to the relation of Eq. (7.58), notice that the interactions allow for an improvement of (7.43) whenever $\mathrm{Tr}\left(H_I[\rho - \tau]\right) + \sum_i \Delta\tilde{F}_{S_i}$ is negative. The expansion of Eq. (7.60) further permits treating each of these terms independently: The terms $\Delta\tilde{F}_{S_i}$ depend only on the local Bloch vector components a_m and b_n, for $i = 1$ and $i = 2$, respectively, whereas the interaction term $\mathrm{Tr}\,(H_I[\rho - \tau])$ depends only on the correlation tensor c_{mn}. With this in mind we can formulate two complementary strategies to improve upon (7.43).

First, we focus on the local terms $\Delta\tilde{F}_{S_i}$. Defining the local Gibbs states as $\gamma_{S_i} \equiv \mathcal{Z}_{S_i}^{-1} e^{-\beta H_{S_i}}$, which are generically different from the local initial states $\tau_{S_1(S_2)} = \mathrm{Tr}_{S_2(S_1)}\,\tau$, it is useful to rewrite $\Delta\tilde{F}_{S_i}$ as,

$$\begin{aligned}\beta\Delta\tilde{F}_{S_i} &= \beta\,(F(\rho_{S_i}) - F(\gamma_{S_i})) - \beta\,(F(\tau_{S_i}) - F(\gamma_{S_i}))\\ &= S(\rho_{S_i}\|\gamma_{S_i}) - S(\tau_{S_i}\|\gamma_{S_i})\,,\end{aligned} \tag{7.63}$$

where $S(\rho\|\tau) = -S(\rho) - \mathrm{Tr}(\rho\ln\tau)$ is the relative entropy. Since $S(\,.\,\|\,.\,)$ is a measure of distinguishability between two quantum states, the quantities $\Delta\tilde{F}_{S_i}$ are negative whenever the final reduced states ρ_{S_i} are closer to the local Gibbs states γ_{S_i} than the initial state marginals τ_{S_i}. This provides a simple strategy to minimize $\Delta\tilde{F}_{S_i}$: The Bloch coefficients $a_m^{(\rho)}$ and $b_n^{(\rho)}$ of the final state ρ should to be chosen as close as possible to $a_m^{(\gamma)}$ and $b_m^{(\gamma)}$, respectively, where $a_m^{(\gamma)} = \frac{d_1}{2}\,\mathrm{Tr}(\gamma_{S_1}\sigma_m^{S_1})$ and $b_n^{(\gamma)} = \frac{d_2}{2}\,\mathrm{Tr}(\gamma_{S_2}\sigma_n^{S_2})$. This strategy ensures that $\Delta\tilde{F}_{S_i} < 0$.

The second strategy entails the minimization of the term $\mathrm{Tr}\,(H_I[\rho - \tau])$. Using Eqs. (7.60) and (7.62), we can express it in terms of the correlation tensors $c_{mn}^{(\rho)}$ and $c_{mn}^{(\tau)}$ of ρ and τ, respectively, obtaining

$$\mathrm{Tr}\,(H_I[\rho - \tau]) = \sum_{m=1}^{d_1^2-1}\sum_{n=1}^{d_2^2-1}\left(c_{mn}^{(\rho)} - c_{mn}^{(\tau)}\right)\epsilon_{mn}\,. \tag{7.64}$$

This relation has a clear geometrical interpretation. Mapping $c_{mn}^{(\rho)}$, $c_{mn}^{(\tau)}$, and ϵ_{mn} to vectors $\mathbf{c}^{(\rho)}$, $\mathbf{c}^{(\tau)}$, and $\boldsymbol{\epsilon}$ in a Euclidean vector space of dimension $(d_1^2 - 1)(d_2^2 - 1)$, the condition of Eq. (7.64) becomes

$$\mathrm{Tr}\,(H_I[\rho - \tau]) = (\mathbf{c}^{(\rho)} - \mathbf{c}^{(\tau)})\cdot\boldsymbol{\epsilon}\,. \tag{7.65}$$

To minimize the expression in (7.65) it is hence desirable to select the vector $(\mathbf{c}^{(\rho)} - \mathbf{c}^{(\tau)})$ to be as antiparallel as possible to $\boldsymbol{\epsilon}$.

The considerations discussed in this section hence provide two complementary strategies to obtain $\beta W < \Delta I_{S_1S_2}$, as desired. In general, the choices of $a_m^{(\rho)}$, $b_m^{(\rho)}$, and $c_{mn}^{(\rho)}$ are limited by the positivity constraint, $\rho \geq 0$ (and of course also by the amount of available work, W). In the next section we illustrate possible issues with the positivity of ρ in more detail for a particular example of two interacting quits.

Improved generation of correlations for two qubits

We consider a system of two qubits, coupled by the Hamiltonian

$$H_S = \omega\, (\sigma_z^{S_1} + \sigma_z^{S_2}) + \epsilon\, \sigma_z^{S_1} \otimes \sigma_z^{S_2}\,, \tag{7.66}$$

where $\omega \geq 0$ and $\epsilon \in \mathbb{R}$ can take either sign. In this simple example, the presence of the interaction Hamiltonian $H_I = \epsilon\, \sigma_z^{S_1} \otimes \sigma_z^{S_2}$ does not change the eigenstates of H_S, but the eigenvalues of the noninteracting system are modified to $(\epsilon \pm 2\omega)$ and $-\epsilon$ (twice degenerate). The initial thermal state $\tau(\beta) = e^{-\beta H_S}/\mathcal{Z}$ is hence of the form

$$\tau(\beta) = \mathcal{Z}^{-1}\, \mathrm{diag}\{e^{-\beta(\epsilon+2\omega)}, e^{\beta\epsilon}, e^{\beta\epsilon}, e^{-\beta(\epsilon-2\omega)}\} \tag{7.67}$$

with $\mathcal{Z} = \mathrm{Tr}\left(e^{-\beta H_S}\right) \geq 0$. The nonzero coefficients of the Bloch decomposition of $\tau(\beta)$ are

$$a_z^{(\tau)} = b_z^{(\tau)} = -2\mathcal{Z}^{-1} e^{-\beta\epsilon} \sinh(2\beta\omega) < 0\,, \tag{7.68a}$$

$$c_{zz}^{(\tau)} = 1 - \frac{4e^{\beta\epsilon}}{\mathcal{Z}}\,. \tag{7.68b}$$

To correlate the system, we apply a two-step protocol based on the strategies discussed before. In the first phase of the protocol, step I, we aim to minimize the term $\mathrm{Tr}\,(H_I[\rho - \tau])$. To do so, we transform the state τ to ρ_{I}, such that the local Bloch vector components remain invariant, $a_z^{(\rho_{\mathrm{I}})} = b_z^{(\rho_{\mathrm{I}})} = a_z^{(\tau)}$, while the (nonzero) correlation tensor coefficient is mapped to

$$c_{zz}^{(\rho_{\mathrm{I}})} = c_{zz}^{(\tau)} - \mathrm{sgn}(\epsilon)\, \alpha_{\mathrm{I}}\,, \tag{7.69}$$

for $\alpha_{\mathrm{I}} \geq 0$. With this, one finds $\mathrm{Tr}\,(H_I[\rho_{\mathrm{I}} - \tau]) = -|\epsilon|\alpha_{\mathrm{I}}$ and from Eq. (7.58) we obtain

$$W_{\mathrm{I}} = T\,\Delta I_{S_1 S_2} - |\epsilon|\alpha_{\mathrm{I}}\,. \tag{7.70}$$

The correlations are hence generated at a work cost that is lower than in the noninteracting case, $W_{\mathrm{I}} \leq T\,\Delta I_{S_1S_2}$. However, it is crucial to note that the transformation in Eq. (7.69) is limited by the positivity constraint, $\rho_I \geq 0$, requiring $2|a_z^{(\tau)}| - 1 \leq c_{zz}^{(\rho_{\mathrm{I}})} \leq 1$. Depending on the sign of the interaction term, one of these bounds is reached, when enough energy is supplied. That is, $c_{zz}^{(\rho_{\mathrm{I}})}$ eventually tends towards either $c_{zz}^{(\rho_{\mathrm{I}})} = 2|a_z^{(\tau)}| - 1$ or $c_{zz}^{(\rho_{\mathrm{I}})} = 1$ for $\epsilon > 0$ or $\epsilon < 0$, respectively.

If more energy is available than is needed to saturate the positivity constraint in step I, we employ the complementary strategy in step II, the second phase of the protocol. Now, we keep the correlation tensor fixed, while changing the local Bloch vector components to minimize $\Delta\tilde{F}_{S_i}$. This entails moving the marginals closer to the states γ_{S_i} that are locally thermal with respect to H_{S_i}. These local Gibbs states are here given by

$$\gamma_{S_i} = \frac{e^{-\beta H_{S_i}}}{\mathcal{Z}_{S_i}} = \frac{1}{2}\,(\mathbb{I} - \tanh(\beta\omega)\sigma_z^{S_i})\ , \tag{7.71}$$

with $a_z^{(\gamma)} = -\tanh(\beta\omega) < 0$. We hence map ρ_{I} to the state ρ_{II} with Bloch vector components given by

$$a_z^{(\rho_{\text{II}})} = (1-\alpha_{\text{II}})\,a_z^{(\tau)} + \alpha_{\text{II}}\,a_z^{(\gamma)}\,, \tag{7.72}$$

where $0 \leq \alpha_{\text{II}} \leq 1$. Again, the positivity constraint $\rho_{\text{II}} \geq 0$ must still be taken into account. For $\epsilon < 0$ we find that the full range of α_{II} is compatible with the positivity of ρ_{II}. The work cost of step II is given by $W_{\text{II}} = T\Delta I_{S_1S_2} + \Delta\tilde{F}_{S_1} + \Delta\tilde{F}_{S_2}$, and, as illustrated in Fig. 7.6, we indeed find that $\Delta\tilde{F}_{S_i} \leq 0$ for all values of $T \geq 0$, $0 \leq \alpha_{\text{II}} \leq 1$, and $\epsilon < 0$.

For $\epsilon > 0$, on the other hand, the positivity constraints require that $|a_z^{(\rho_{\text{II}})}| \leq |a - z^{(\tau)}|$. Since $a_z^{(\tau)} < 0$ and $a_z^{(\gamma)} = -\tanh(\beta\omega) < 0$, Eq. (7.72) yields $|a_z^{(\rho_{\text{II}})}| = (1-\alpha_{\text{II}})|a_z^{(\tau)}| + \alpha_{\text{II}}\tanh(\beta\omega) \geq |a_z^{(\tau)}|$. Unfortunately, since $|a_z^{(\tau)}| = \sinh(2\beta\omega)/\left(\cosh(2\beta\omega) + e^{-\beta\epsilon}\right) \leq \tanh(\beta\omega)$, one finds that $|a_z^{(\rho_{\text{II}})}| \geq |a - z^{(\tau)}|$, that is, the positivity constraint does not allow for step II of the protocol to be carried out for $\epsilon > 0$.

In addition to the strategies discussed here, the states obtained after steps I and II may be further correlated until the maximal value of correlation is reached. However, the work cost per newly generated unit of correlation beyond this point may be the same, or even higher than in the noninteracting case.

7.7. Concluding remarks

We have studied the possibility of generating correlations, and in particular entanglement, in thermal environments. We have investigated how the initial temperature limits the amount of correlations that can be generated. In particular, we have worked out fundamental limitations in terms of upper bounds to the possibility to create entanglement at finite temperature. Furthermore we have also obtained lower bounds by introducing explicit protocols, which can, remarkably, reach the upper bounds in some cases. In the multipartite setting

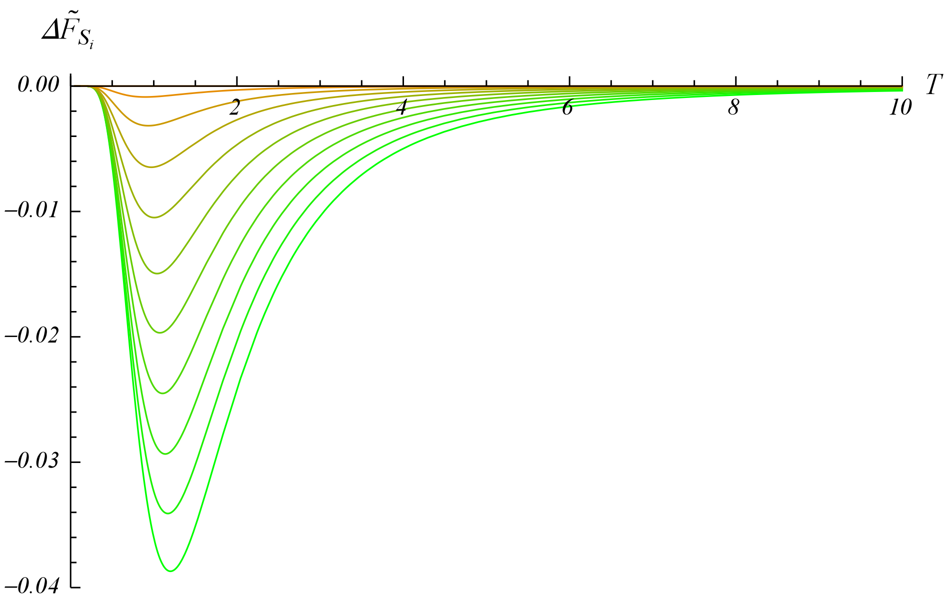

Figure 7.6.: Advantage in correlation cost: During step II of the protocol to generate correlations between two qubits, an advantage over the noninteracting case arises when $\Delta\tilde{F}_{S_i}$ from Eq. (7.59) becomes negative. $\Delta\tilde{F}_{S_i}$ is plotted here against the temperature T in units of ω (recall that we use units where $\hbar = k_{\mathrm{B}} = 1$) for $\alpha_{\mathrm{II}} = 0.5$, and the different curves correspond to values of ϵ (also in units of ω) from $\epsilon = 0$ (top) to $\epsilon = -1$ (bottom) in steps of 0.1. The advantage increases with increasing coupling strength ϵ, but does not monotonically decrease with the temperature. Instead, the advantage becomes maximal at a finite temperature. Although curves are only shown for a fixed value $\alpha_{\mathrm{II}} = 0.5$, we have checked that other values yield analogous behaviour and the advantage increases monotonically with α_{II}.

we studied the advantage of having more systems at one's disposal, providing an explicit route to overcome some of the fundamental limitations.

In a second step we have worked out the energy cost of creating correlations and entanglement, highlighting the interplay between quantum effects and thermodynamic resources. In the bipartite setting we managed to provide explicit protocols which yield an upper bound to the work cost of creating a unit of correlation or an e-bit (a fundamental unit of entanglement). We have also explored the possibility of performing transformations using an auxiliary thermal bath at the same temperature, in which case the relation between work and units of correlations takes a very simple form: $W \geq T I_{S_1 S_2}$. That is, in order to create I units of correlations, we need to invest at least an amount TI units of work. We have developed a simple protocol saturating this bound, and discussed its validity in the case of interacting Hamiltonians.

The different protocols and upper bounds introduced in this chapter, both in terms of limiting temperatures and energy costs, serve as ultimate bounds on the possibilities of information processing in scenarios where thermodynamic considerations cannot be ignored. Finally, from a more theoretical point of view, our results establish a link between fundamental resources of two theories: entanglement theory (HHHH09) and the resource theory of thermodynamics (BaHO^{+}13).

8. Work and entropy production with Generalized Gibbs Ensembles

8.1. Introduction

Gibbs states, being the only completely passive states, play a fundamental role in quantum thermodynamics. In fact, most often they are taken for granted: For example, in the resource theory of thermodynamics, they are considered as a free resource, and one is concerned in studying the transformations allowed by thermal operations. Similarly, in the study of thermal heat engines, heat baths are initially prepared in thermal states, and any system (weakly) interacting with the bath is assumed to evolve towards a Gibbs states at the same temperature as the bath.

In parallel with these studies, a second branch of quantum thermodynamics is emerging: This is the study of quantum many-body systems out of equilibrium and the question of thermalisation (CC06; CDEO08; RDO08; LPSW09; SF12; Rei08; CE13). In this context, thermal baths are by no means assumed to be available: Instead, one of the main goals of this field of research is to find out under what precise conditions closed many-body systems are expected to thermalise and —as one often says —"form their own heat bath". Despite remarkable progress in recent years, many questions on many-body systems out of equilibrium remain open, even understanding whether non-integrable generic systems always thermalise (GE15). Many-body localised systems are expected not to thermalise, as they keep memory of the initial conditions, while integrable models do not equilibrate to Gibbs states, but to the so-called generalised Gibbs ensembles (GGE) (CDEO08; CCR11; CE13; PE09; FE13; CEF12; ZMP15; INW^{+}15). For comprehensive reviews on the subject, see, e.g., Refs. (EFG15; PSSV11; GE15; DKPR15).

The purpose of the following chapter is to bring these two realms of study closer together, and study entropy production and work extraction taking into account these recent insights into the mechanism of equilibration in many-body systems. Stated otherwise, we want to study quantum thermodynamics in situations where Gibbs states are not necessarily the right description of the equilibrium state.

More specifically, in this chapter we consider a closed system that undergoes a sequence of quenches and relaxations to an equilibrium state. Importantly, unlike in standard studies in thermodynamics, equilibration after each quench does not occur through weak coupling with an external (infinite) thermal bath. In contrast, we incorporate the equilibration towards statistical ensembles as an effective description of the unitary evolution of the closed system. This effective description is adequate to describe the system only for a restricted, although most relevant, set of observables. We consider three kinds of equilibrium states: the time averaged state, the Gibbs ensemble, and the generalised Gibbs ensemble. Work extraction and entropy production will be studied for these three models of equilibration, when either local quenches in a sub-region of the many body system, or global quenches are performed. Finally, we will study in detail a particular physical system well described by the GGE, namely free fermionic systems.

It is also important to put this chapter in context with the previous ones. In chapters 3 and 4, we studied work extraction assuming complete control over the system, as we considered the ability to implement arbitrary unitary operations. Here we take a more constrained set of operations, by only allowing two physically relevant types of evolutions,

- *Quenches*, i.e., fast controlled transformation of the Hamiltonian.
- *Equilibrations,* i.e., free (uncontrolled) evolution of the system.

Despite their simplicity, these two operations are enough to characterise the optimal protocols for work extraction described in Chapter 4 (Abe13). Furthermore, they provide a clean way to distinguish between controlled and non-controlled degrees of freedom, which allows us to speak about entropy production in closed systems. Indeed, entropy production will be associated with our continuous loss of information due to the equilibration processes. We also relate entropy production with the velocity of the work extraction process, and study the minimal work principle (AN05b). We show that its range of validity can depend strongly on the model of equilibration.

This Chapter is structured as follows. In Sec. 8.2 we introduce the three models of equilibration we consider and discuss its physical relevance as a description of the effective evolution of closed many-body systems. In Sec. 8.3 we turn to presenting our framework of work extraction based on quenches and equilibrations. Sec. 8.4 discusses notions of entropy production in each of the models of equilibration, where we introduce rigorous conditions for the absence of entropy production and carefully relate these conditions to notions of reversible processes. In Sec. 8.6 we discuss the minimal work principle and the protocols for optimal work extraction for each of the models of equilibration. Lastly, in Sec. 8.8 we study numerically a model of non-interacting fermionic systems, where many of the features throughout our theoretical analysis are emerging. The results of this Chapter are original and can be found in (PLRG^{+}15).

8.2. Equilibration models

When referring to equilibration of quantum many-body systems, we refer to finite but large systems. Such closed quantum many-body systems cannot truly equilibrate due to their unitary evolution. What is generically the case, however, is that expectation values of large restricted sets of observables equilibrate in time to the value attained for the time average (Rei08; Rei12; Sho11; CDEO08), in the sense that they stay close to the time average for most times. This is particularly true for local observables (GPLM^{+}15).

8.2.1. Time average state or diagonal ensemble

We say that an observable A equilibrates if, after some relaxation time, its expectation value is for most times the same $\langle A(t)\rangle \simeq \mathrm{Tr}(A\omega)$ as the expectation value of the *infinite time average*

$$\omega(\rho, H) := \lim_{T\to\infty} \frac{1}{T}\int_0^T e^{-\mathrm{i}Ht}\,\rho\, e^{\mathrm{i}Ht}\mathrm{d}t\,, \tag{8.1}$$

of an initial state ρ of a system described by a Hamiltonian H. A simple calculation shows that the time averaged state corresponds to the de-phased state in the energy basis and for this reason is often called *diagonal ensemble.* More explicitly, if H is given by,

$$H = \sum_k E_k P_k \tag{8.2}$$

then the time averaged state reads

$$\omega(\rho, H) = \sum_k P_k \rho P_k\,. \tag{8.3}$$

It is interesting to note that the time averaged state corresponds to the maximum entropy state given all the conserved quantities (GME11). This observation turns the *principle of maximum entropy* introduced by Jaynes (Jay57) into a consequence of the quantum dynamics. The principle of maximum entropy states that the probability distribution which best represents the current state of knowledge of the system is the one with largest entropy given the conserved quantities of the system and it will be crucial to define our equilibration models.

Although relaxation towards the time averaged state has been proven under very general conditions (Rei08; LPSW09; SF12; Rei12), in practice, the diagonal ensemble cannot be used as an equilibration model due to its inefficiency. The description of the equilibrium state by the diagonal ensemble requires the specification of as many conserved quantities as the dimension of the Hilbert space, which scales exponentially in the system size. It is therefore not even possible in principle to write save all the data in a computer for a large interacting many-body system.

8.2.2. Canonical or Gibbs ensemble

In practice, the characterisation of the equilibrium state can in many instances be done by specifying only a few quantities, e.g., the temperature and the chemical potential. The most relevant and common case is the *canonical ensemble* or the *Gibbs state*, for which only the temperature, or equivalently the energy per particle of the initial state ρ, has to be specified,

$$\omega_{\text{Gibbs}}(\rho, H) = \frac{e^{-\beta H}}{Z}\,, \tag{8.4}$$

where ρ is the state of the system before undergoing the equilibration process, $Z = \text{Tr}(e^{-\beta H})$ is the partition function and the inverse temperature $\beta > 0$ is fixed by imposing that $\text{Tr}(H\omega_{\text{Gibbs}}) = \text{Tr}(H\rho)$.

For generic, non-integrable models, the thermal state is expected to be indistinguishable from the time averaged state under very mild assumptions on the Hamiltonian (Sre94; RDO08; GE15) and on the energy distribution of the initial state (RGE12; BC15). While the dynamical thermalisation has not been rigorously proven, it is highly plausible, and it can be connected to typicality arguments (PSW06; GLTZ06). The generality of these conditions explains why the canonical ensemble is the corner-stone of the standard thermodynamics. Nevertheless, there are known instances of systems that do not thermalise. One central aim of this work is to study *how the laws of thermodynamics are modified when the Gibbs ensemble is not a good equilibration model and does not satisfactorily describe the equilibrium state of the system.*

8.2.3. Generalised Gibbs ensemble

Examples of systems which do not fully thermalise to Gibbs states are constituted by *integrable systems.* The infinite-time averaged states are not well described by the Gibbs ensemble because of the existence of (quasi) local integrals of motion, i.e., conserved quantities Q_i that retain an infinite memory about the initial state. In this case, the equilibrium states can be well-described by the so-called generalised Gibbs ensemble (GGE) defined as

$$\omega_{\mathrm{GGE}}(\rho, H, \{Q_i\}) \propto e^{-\beta H+\sum_{j=1}^{m}\lambda_j Q_j} \tag{8.5}$$

where the generalised chemical potential λ_j is a Lagrange multiplier associated to the specific conserved quantity Q_j, $j = 1, ..., m$, such that its expectation value is the same as the one of the initial state

$$\mathrm{Tr}\left(\omega_{\mathrm{GGE}}(\rho, H, \{Q_i\})Q_k\right) = \mathrm{Tr}(\rho Q_k)\,. \tag{8.6}$$

for each $k = 1, ..., m$. The GGE can be understood as an interpolation between the diagonal and the canonical ensembles. The diagonal ensemble maximises the von Neumann entropy $S(\rho) = -\mathrm{Tr}(\rho \log \rho)$ given all the conserved quantities $\{P_k\}$. The Gibbs ensemble maximises the von Neumann entropy considering only the energy as a conserved quantity. The GGE is situated in between. For a given state ρ and a set of operators (conserved quantities) $\{Q_i\}$, it is natural to define the set of states compatible with the values the conserved quantities

$$\mathcal{E}(\rho, \{Q_i\}) := \{\sigma |\, \mathrm{Tr}(\rho Q_i) = \mathrm{Tr}(\sigma Q_i)\}. \tag{8.7}$$

The GGE is the state that maximises the von Neumann entropy within $\mathcal{E}(\rho, \{Q_i\})$. From this perspective, the ensembles introduced so far can be summarised as

$$\omega(\rho, H) := \mathrm{argmax}_{\sigma\in\mathcal{E}(\rho,\{P_k\})} S(\sigma)\,, \tag{8.8}$$

$$\omega_{\mathrm{GGE}}(\rho, H, \{Q_i\}) := \mathrm{argmax}_{\sigma\in\mathcal{E}(\rho,\{H,Q_i\})} S(\sigma)\,, \tag{8.9}$$

$$\omega_{\mathrm{Gibbs}}(\rho, H) := \mathrm{argmax}_{\sigma\in\mathcal{E}(\rho,\{H\})} S(\sigma)\,. \tag{8.10}$$

Let us note that the entropy of the time averaged state has been introduced in Ref. (Pol11) as the *diagonal entropy*, where this quantity is argued to extend the thermodynamic entropy in out-of-equilibrium quantum systems. A relevant question in the construction of GGEs is how the conserved quantities have to be chosen, and there is a certain degree of ambiguity of what constants of motion to pick in order to arrive at the appropriate equilibrium state (GE15). This discussion is not relevant for the general study pursued in this chapter, however. It is the aim of our work to study the thermodynamical behaviour of the GGE in full generality, hence we will not have to make any precise assumption about the conserved quantities, unless it is explicitly specified.

8.2.4. Example: Equilibration of a quadratic fermionic model

To illustrate the above considerations, let us consider a quadratic Hamiltonian of fermions in a one dimensional lattice,

$$H^{(0)} = \sum_{i=1}^{n} \epsilon_i a_i^\dagger a_i + \sum_{i=1}^{n-1} g \left(a_i^\dagger a_{i+1} + a_{i+1}^\dagger a_i \right), \tag{8.11}$$

where n is the total number of sites and a_i ($a_i^\dagger$) are the creation (annihilation) operators in the i-site, which satisfy the fermionic anti-commutation relations $\{a_i, a_i^\dagger\} = \delta_{i,j}$ and $\{a_i, a_j\} = \{a_i^\dagger, a_j^\dagger\} = 0$. We would like to study how an initially out of equilibrium state relaxes to equilibrium and see that the Gibbs ensemble fails to describe the equilibrium state.

The initial state of the system is taken to be in thermal equilibrium,

$$\rho^{(0)} = e^{-\beta H^{(0)}} / \mathcal{Z} \tag{8.12}$$

A quench is then performed to a new Hamiltonian $H^{(1)}$, $H^{(0)} \mapsto H^{(1)}$, in which the energy of the first fermion is modified,

$$H^{(1)} = H^{(0)} + \Delta a_1^\dagger a_1. \tag{8.13}$$

After the quench, the population of the first fermion evolves in time as,

$$n_1(t) = \mathrm{Tr}(a_1^\dagger a_1 \rho(t)) \tag{8.14}$$

with $\rho(t) = e^{-\mathrm{i} H^{(1)} t} \rho(0) \, e^{\mathrm{i} H^{(1)} t}$. As the Hamiltonian is quadratic, it can be exactly diagonalized, and the time evolution can be exactly simulated for large times and system sizes (the difficulty of the problem scales linearly with n instead of exponentially). This is explained in detail in Appendix A.5.

In Fig. 8.1, we plot the time evolution of the occupation of the first site $n_1(t)$. As expected, we see that after some relaxation time, $n_1(t)$ equilibrates to the value predicted by the GGE—which is relatively far from the one given by the Gibbs equilibration model. The situation described in this example, a quench and the characterisation of the equilibrium state, is extensively studied in the literature, see for a recent review (GE15). One of the goals of this work *is to define and study the suitability of effective descriptions in terms of GGE states for processes where many quenches are performed.*

8.3. Framework for thermodynamic protocols

In the previous section we have introduced the different equilibration models that describe the equilibrium state that is reached when a system initially in

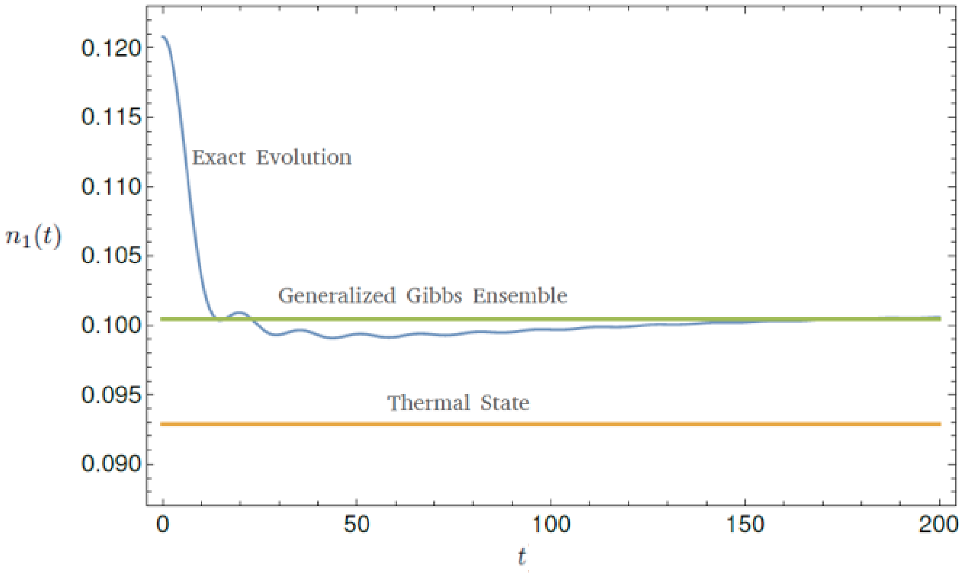

Figure 8.1.: Time evolution of the occupation of the first site of the lattice $n_1 = a_1^\dagger a_1$ for a quadratic Hamiltonian of n fermions in a one dimensional lattice. For the example we take $n = 100$, $\epsilon_i = 1$, $\Delta = 0.15$, $\beta = 2$, $g = 0.1$ and time is measured in units of $1/(10g)$. An equilibration around the GGE is observed, even for this moderately sized quantum system.

state ρ evolves under Hamiltonian H. By construction, these models can be used to describe the equilibrium state that is reached when a system in state ρ and with initial Hamiltonian $H^{(\mathrm{ini})}$ undergoes a quench $H^{(\mathrm{ini})} \mapsto H^{(\mathrm{fin})}$ and later the system evolves under the final Hamiltonian $H^{(\mathrm{fin})}$ for a sufficiently long time. In this case, the equilibrium state will be described by

$$\begin{aligned}
&\omega(\rho, H^{(\mathrm{fin})}) := \operatorname{argmax}_{\sigma \in \mathcal{E}(\rho, \{P_k^{(\mathrm{fin})}\})} S(\sigma)\,, \\
&\omega_{\mathrm{GGE}}(\rho, H^{(\mathrm{fin})}, \{Q_i^{(\mathrm{fin})}\}) := \operatorname{argmax}_{\sigma \in \mathcal{E}(\rho, \{H, Q_i^{(\mathrm{fin})}\})} S(\sigma)\,, \\
&\omega_{\mathrm{Gibbs}}(\rho, H^{(\mathrm{fin})}) := \operatorname{argmax}_{\sigma \in \mathcal{E}(\rho, \{H^{(\mathrm{fin})}\})} S(\sigma)\,.
\end{aligned}$$

However, thermodynamic processes (for instance a protocol of work extraction) often involve a series of quenches and equilibrations. We will now extend our previous considerations to such processes involving sequences of quenches and equilibrations.

8.3.1. Equilibration under repeated quenches

Consider a sequence of changes of the Hamiltonian, as defined by a list of $N+1$ Hamiltonians, $H^{(m)}$, where $m = 0, 1, \ldots, N$ denotes the step in the protocol and $H^{(0)}$ is the initial Hamiltonian. These Hamiltonian transformations $H^{(m-1)} \mapsto H^{(m)}$ are considered to be *quenches*, in the sense that they are performed sufficiently fast such that the state of the system ρ is unchanged. Let us denote the time at which the quench $H^{(m-1)} \mapsto H^{(m)}$ is performed by t_m with $t_m < t_{m+1}$ for all m. After a quench, the system evolves under the Hamiltonian $H^{(m)}$ for a time $t_{m+1} - t_m$ until a new quench $H^{(m)} \mapsto H^{(m+1)}$ is performed at time t_{m+1}. This time interval is taken to be much longer than the equilibration time such that the system can be considered to be in equilibrium. The exact state of the system $\rho(t)$ when m quenches have taken place ($t_m < t < t_{m+1}$) is given by,

$$\rho(t) = e^{-i(t-t_m)H^{(m)}} \rho(t_m) e^{i(t-t_m)H^{(m)}}, \tag{8.15}$$

where $\rho(t_m)$ is the state of the system at $t = t_m$ when the Hamiltonian $H^{(m)}$ starts to dictate the evolution. The state $\rho(t_m)$ is given by the recursive expression

$$\rho(t_k) = e^{-i(t_k - t_{k-1})H^{(k-1)}} \rho(t_{k-1}) e^{i(t_k - t_{k-1})H^{(k-1)}}\,. \tag{8.16}$$

Now, our aim is to construct an effective description of the whole evolution of ρ, in such a way that the state after the m-th quench and its posterior equilibration, $\rho(t)$, can be described by an appropriate equilibrium state. We denote such equilibrium state that approximates the real state after m quenches, $\rho(t)$, as $\omega^{(m)}_{(\cdots)}$ where $(\cdots)$ is the place holder for one of the three models of equilibration: time-average (TA), GGE or Gibbs. The effective description of (8.15) is then built in a recursive way as follows,

$$\begin{aligned}
\omega^{(m)}_{\text{TA}} &= \omega\big(\omega^{(m-1)}_{\text{TA}}, H^{(m)}\big),\\
\omega^{(m)}_{\text{GGE}} &= \omega_{\text{GGE}}\big(\omega^{(m-1)}_{\text{GGE}}, H^{(m)}, \{Q^{(m)}_i\}\big),\\
\omega^{(m)}_{\text{Gibbs}} &= \omega_{\text{Gibbs}}\big(\omega^{(m-1)}_{\text{Gibbs}}, H^{(m)}\big).
\end{aligned} \tag{8.17}$$

Here, $\omega^{(0)}_{(\cdots)} = \rho(t_0)$ is the intial state, before any quench or evolution has taken place. Note that, when constructing the GGE description, the set of conserved quantities $\{Q^{(m)}_i\}$ changes for every Hamiltonian $H^{(m)}$.

In order to provide a motivation and interpretation of Eq. (8.17), together with the implicit assumptions that come into play, let us illustrate it with a simple example. Suppose a system initially in state $\rho(0)$ and with Hamiltonian $H^{(0)}$. At time t_1, we perform a first quench $H^{(0)} \mapsto H^{(1)}$ and let the system evolve under $H^{(1)}$; at time t_2 we perform second quench $H^{(1)} \mapsto H^{(2)}$ and let the system evolve under $H^{(2)}$ until it equilibrates at time t. For both evolutions, we now consider effective descriptions in terms of GGE states. After the fist evolution and immediately before performing the second quench, the system is exactly described by $\rho(t_2)$ as given by Eq. (8.16). For a set of conserved quantities $\{Q^{(1)}_i\}$, the corresponding GGE equilibrium state is given by,

$$\omega^{(1)}_{\text{GGE}} = \omega_{\text{GGE}}\big(\rho(t_1), H^{(1)}, \{Q^{(1)}_i\}\big) \simeq \rho(t_2), \tag{8.18}$$

where the symbol "$\simeq$" means in this context that the average value of relevant observables is well approximated by $\omega^{(1)}_{\text{GGE}}$, that is

$$\text{Tr}(A\rho(t_2)) \simeq \text{Tr}(A\omega^{(1)}_{\text{GGE}}). \tag{8.19}$$

Now, when describing the equilibrium state after the second quench, one can simply apply the same recipe. That is, the state $\rho(t^{(1)})$ is the initial state when the evolution under $H^{(2)}$ starts. Then, assuming that the new conserved quantities $\{Q^{(2)}_i\}_i$ are chosen appropriately and applying the same reasoning one obtains an approximation by taking

$$\omega_{\text{GGE}}\big(\rho(t_2), H^{(2)}, \{Q^{(2)}_i\}\big) \simeq \rho(t), \tag{8.20}$$

with t longer than the t_2 plus the subsequent equilibration time. Importantly, note that this effective description is not efficient, in the sense that it requires keeping track of the exact state $\rho(t_2)$ to obtain the equilibrium state at time t. If this is extended to N quenches, having to keep track of the exact evolution until the $(N-1)$-th quench is as demanding as keeping track of the whole exact evolution over the process. It is here when the effective description (8.17) becomes handy, as it can be constructed by keeping track of the value of the conserved quantities only. First of all, coming back to the first evolution, note that by applying (8.17) with $m=1$ we recover (8.18), i.e., the standard result for single quenches. Now, in order to construct the GGE state corresponding to $\rho(t)$, we assume that the conserved quantities $\{Q_i^{(2)}\}$ are within the set of physically relevant observables A in (8.19). That is, we assume that

$$\mathrm{Tr}(Q_i^{(2)}\rho(t_2)) \simeq \mathrm{Tr}(Q_i^{(2)}\omega_{\mathrm{GGE}}^{(2)}) \tag{8.21}$$

for all i. In this way, in order to obtain the equilibrium GGE ensemble after the second quench, it is not necessary to keep track of the exact state $\rho(t_2)$, but one can simply use $\omega_{\mathrm{GGE}}^{(1)}$ instead. Using (8.21) we then obtain,

$$\begin{aligned}
\omega_{\mathrm{GGE}}^{(2)} &:= \omega_{\mathrm{GGE}}\big(\omega_{\mathrm{GGE}}^{(1)}, H^{(2)}, \{Q_i^{(2)}\}\big) \\
&\simeq \omega_{\mathrm{GGE}}\big(\rho(t_2), H^{(2)}, \{Q_i^{(2)}\}\big) && (8.22)\\
&\simeq \rho(t). && (8.23)
\end{aligned}$$

Extending the same reasoning to the case of N quenches and other models of equilibration other than the GGE, we arrive an effective description of the form (8.17).

In the rest of this Chapter we will always use the effective description (8.17) for the full process, in full analogy to what is usually done in thermodynamics by always using the Gibbs state as a description for equilibrium states. We thereby make the assumption that possible small errors in the effective description do not accumulate under repeated quenches. In Sec. 8.8 we provide a numerical comparison of the real exact evolution and the model of Eq. (8.17) for the case of free fermions. We will show for this example that the model predicts with great accuracy the amount of work that is extracted in a protocol involving a sequence of quenches. We leave as an open problem to identify both numerically and analytically for which systems and protocols it is possible to apply recursively the time-average, GGE or Gibbs models of equilibration as we do in this work and it is canonically done in thermodynamic protocols for the usual Gibbs ensemble.

8.3.2. Work cost of quenches

Concatenations of quenches and equilibrations constitute a framework to describe thermodynamic processes -see, e.g., Refs. (Abe13; AG13). Within this framework, work is associated with the input energy under quenches, whereas heat is associated with the exchange of energy under equilibration processes. At the level of average quantities, the work cost of a single quench, $H^{(m-1)} \mapsto H^{(m)}$, reads

$$W^{(m)} := \mathrm{Tr}\left(\rho(t_m)(H^{(m)} - H^{(m-1)})\right) \tag{8.24}$$

where $\rho(t_m)$ is given in (8.15). The main assumption of this work is precisely that the work cost of a quench is very well approximated by the effective description of the equilibrium state, i. e.

$$W^{(m)} = \mathrm{Tr}\left(\omega^{(m-1)}(H^{(m)} - H^{(m-1)})\right) , \tag{8.25}$$

where $\omega^{(m-1)}$ is its effective description (8.17). As the equilibration processes happen spontaneously and have no work cost, the total work extracted in the entire protocol is simply given by the sum of the steps

$$W := \sum_{i=1}^{N} W^{(m)}. \tag{8.26}$$

8.3.3. The system - bath set-up

A particularly relevant scenario is the system - bath setting. We call system S to the part of the total system upon which one has control and it is possible to quench its Hamiltonian H_S. The bath B contains the degrees of freedom upon one has no control and it is the responsible for equilibrating the system S. In order for this equilibration to happen, the dimension of the Hilbert-space of S, $\dim(\mathcal{H}_S)$, is considered to be much smaller than that of the bath,

$$\dim(\mathcal{H}_S) \ll \dim(\mathcal{H}_B). \tag{8.27}$$

and the total Hamiltonian to be of the form,

$$H^{(m)} = H_S^{(m)} \otimes \mathbb{1}_B + \mathbb{1}_S \otimes H_B + V. \tag{8.28}$$

where the interaction V is supported on S and B and couples the two subsystems. Unlike the standard assumptions in thermodynamics, we do not assume that the interaction V is weak or that bath size is infinite.

8.4. Entropy production and reversible processes

8.4.1. Notions of entropy production

An important quantity in thermodynamic processes is the entropy production on system and bath during the protocol. Of course, the exact unitary dynamics on SB does not change the von Neumann entropy in the system. However, we are using an effective description on SB and in this effective description the entropy might well change. This allows us to study entropy production in such an effective description, which may be given in terms of time average states, GGE states, or Gibbs states, depending on the context. In this section we study general properties of such an entropy production, and show that it tends to zero in quasi-static processes, as expected from phenomenological thermodynamics.

First of all, note that due to the fact the equilibration models can all be understood as a maximisation of the entropy given some constraints, it follows that the entropy of the effective description $\omega^{(i)}$ of SB is non-decreasing during a thermodynamic protocol

$$S(\omega^{(i+1)}) \geq S(\omega^{(i)}) \quad \forall i = 0, \dots, N. \tag{8.29}$$

Therefore, thermodynamic protocols are in general irreversible: If we start with the final state of the protocol and then run the protocol backwards, we will in general not end up with the original initial state.

From phenomenological thermodynamics we would expect that the protocols become reversible if they are done in a quasi-static way. In the context of our set of operations, a quasi-static process is defined by considering $N \to \infty$ quenches $H^{(i)} \mapsto H^{(i+1)}$ such that $H^{(i+1)} - H^{(i)}$ is of order $1/N$, followed each by an equilibration process. We will now discuss in detail in which sense such a statement remains true.

For our discussion let $\alpha \mapsto H(\alpha)$ with $\alpha \in [0,1]$ be a smooth path of Hamiltonians. For a fixed N we can discretise it as $H^{(i)} = H(i/N) = H(\alpha)$ and therefore we can meaningfully speak about limits of slower and slower protocols as $N \to \infty$. It has to be clear, however, that even for small N, the protocols might take a considerably large time, as we assume an equilibration process after each quench. We will denote by $\omega(\alpha) \equiv \omega^{(i)}$ the equilibrium state after the ith quench, and $S(\alpha)$ its entropy.

8.4.2. Entropy production for time averaged ensembles

As a first result, let us show that there is no entropy production in a quasi-static process ($\delta\alpha \equiv 1/N \to 0$) when the equilibrium states are described by the time average state (8.1) -i.e., when all conserved quantities are taken into account. To show this result, we write the eigenvalues $p_k(\alpha+\delta\alpha)$ of the density matrix after the $i+1$th quench in terms of the eigenvalues of $\omega(\alpha)$, as

$$\begin{aligned} p_k(\alpha+\delta\alpha) &= \langle E_k(\alpha+\delta\alpha)|\omega(\alpha)|E_k(\alpha+\delta\alpha)\rangle \\ &= \sum_{k'} p_k(\alpha)|\langle E_{k'}(\alpha)|E_k(\alpha+\delta\alpha)\rangle|^2, \end{aligned} \tag{8.30}$$

where we have used that the eigenvalues of $\omega(\alpha+\delta\alpha)$ are simply the diagonal elements of $\omega(\alpha)$ in the basis given by $|E_k(\alpha+\delta\alpha)\rangle$. Let us now assume differentiability of the eigenbasis, i.e.,

$$|E_k(\alpha+\delta\alpha)\rangle = \frac{1}{\sqrt{1+\delta\alpha^2}}\left(|E_k(\alpha)\rangle + |X_k(\alpha)\rangle\delta t\right), \tag{8.31}$$
$$\langle X_k(\alpha)\,|X_k(\alpha)\rangle = 1, \quad \langle E_k(\alpha)\,|X_k(\alpha)\rangle = 0.$$

Then we get

$$\begin{aligned} p_k(\alpha+\delta\alpha) &= p_k(\alpha)\frac{1+\delta\alpha^2\sum_{k'\neq k}|\langle E_{k'}(\alpha)\,|X_{k'}(\alpha)\rangle|^2}{1+\delta\alpha^2} \\ &= p_k(\alpha) + O(\delta\alpha^2) \text{ as } \delta\alpha\to 0. \end{aligned} \tag{8.32}$$

This implies that the populations of the density matrix of the system are constant in the slow process limit $\delta\alpha\to 0$. Hence, it follows that the entropy of the (diagonal) time-averaged state is constant.

8.4.3. Entropy production for time generalised Gibbs ensembles

Now, we consider the case of a generic GGE equilibration where not all the conserved quantities are taken into account. In this case, the equilibration model (8.17) satisfies the relation,

$$\mathrm{Tr}\left(\omega_{GGE}^{(m)}Q_i^{(m)}\right) = \mathrm{Tr}\left(\omega_{GGE}^{(m-1)}Q_i^{(m)}\right), \tag{8.33}$$

for all $i=1,\dots,m$. Here the $Q_i^{(m)}$ correspond to the conserved quantities of $H^{(m)}$, and Eq. (8.33) determines the corresponding Lagrange multipliers $\lambda_i^{(m)}$ in (8.5). For such equilibrium states, we also identify conditions so that there is no entropy production.

More precisely, we find the following result: If the Lagrange-multipliers as determined by (8.33), form in the limit $N\to\infty$ a set of smooth functions

$\alpha \mapsto \lambda_j(\alpha)$ for $j = 1, \ldots, m$, then the entropy is preserved in such a quasi-static process. This result is shown simply by taking the continuum limit of eq. (8.33) which yields

$$\mathrm{Tr}\left(\frac{\mathrm{d}\omega(\alpha)}{\mathrm{d}\alpha} Q_j(\alpha)\right) = 0, \quad \forall j = 1, \ldots, m \tag{8.34}$$

which can be in turn used to show that the entropy production vanishes,

$$\frac{\mathrm{d}S}{\mathrm{d}\alpha} = \sum_{j=1}^{m} \lambda_j(\alpha)\, \mathrm{Tr}\left(\frac{\mathrm{d}\omega(\alpha)}{\mathrm{d}\alpha} Q_j(\alpha)\right) = 0. \tag{8.35}$$

Let us now discuss heuristically under which conditions we expect that $\{\lambda_j\}_1^m$ are smooth functions. This can be well illustrated by the following example: Consider the case of a two dimensional system for which we take $m = 1$, that is, the only conserved quantity is the Hamiltonian $Q_1 = H$ itself (i.e., the Gibbs equilibration model). Consider initially a non-degenerate Hamiltonian

$$H(0) = E|1\rangle\langle 1| \tag{8.36}$$

and an arbitrary initial state $\rho(0)$ with an inverse temperature $\beta(0) > 0$ and thus the entropy is smaller than $\log(2)$. Now suppose that the final Hamiltonian

$$H(1) = 0 \tag{8.37}$$

has degenerate energy levels. Now take as a Hamiltonian path

$$H(\alpha) = E(1-\alpha)|1\rangle\langle 1| = H(0)(1-\alpha) \tag{8.38}$$

and an initial Gibbs state with inverse temperature $\beta(0)$. Then the eigenbasis in the entire process does not change. Now note that the condition (8.33) implies that the energy is preserved in every equilibration. But since we are dealing with a two-dimensional system, as long as $H(\alpha)$ is non-degenerate, the state itself will remain constant $\omega(\alpha) = \rho(\alpha)$ for any $\alpha \in [0, 1)$. In order to keep the state constant, the inverse temperature needs to fulfil

$$\beta(\alpha) = \beta(0)/(1-\alpha). \tag{8.39}$$

Therefore, the inverse temperature $\beta(\alpha) \to \infty$ as $\alpha \to 1$, and it necessarily diverges as $\alpha \to 1$. Note that, in this case, when one reaches $H(1)$, the final state is a maximally mixed state with entropy $\log(2)$, which is larger than the one of the initial state by assumption.

Intuitively speaking, this example is easy to understand. Given that the final Hamiltonian $H(1)$ has two degenerate levels, any Gibbs states will have entropy at least given by $\ln 2$. Hence, if we take as an initial state one with entropy lower than $\ln 2$, and choose and effective description in terms of Gibbs states, entropy will necessarily be generated. The way to make this example compatible with our previous result is to realise that the Lagrange multipliers become infinite in this case. As a final remark, it is important to note that in this case, our effective description (in terms of Gibbs states) differs from the description in terms of time averaged states -which is expected to be the exact one.

The previous example shows that in some cases the premise of our result is not fulfilled. However, these pathological cases often imply that the chosen GGE description is not accurate. For example, in the case of encountering a ground state degeneracy, any conserved quantity in the GGE that discerns the ground states would be enough to fix the problem. However, we leave in general open whether one can find smooth trajectories for $t \mapsto \lambda_j(\alpha)$ for a given set of conserved quantities and trajectory of Hamiltonians—this may well depend on the specifics of the model and on the ambiguity of what constants of motion to pick in the first place (GE15).

8.4.4. Entropy production for Gibbs ensembles

Nonetheless, we can provide a definite answer to this problem in the case of the Gibbs equilibration model (where the energy is the only conserved quantity). Here we can show that: Given a quasi-static trajectory of Hamiltonians $H(\alpha)$ and initial state $\rho(0) = e^{-\beta(0)H(0)}/Z$; if there exists *any* smooth function $\alpha \mapsto f(\alpha) \neq 0 \,\forall \alpha$ with $f(0) = \beta(0)$ such that

$$S\left(\frac{e^{-f(\alpha)H(\alpha)}}{Z}\right) = S(\rho(0)) \tag{8.40}$$

then the quasi-static process along $\alpha \mapsto H(\alpha)$ has no entropy production.

Defining the family of states

$$\omega_f(\alpha) := \frac{e^{-f(\alpha)H(\alpha)}}{Z}, \tag{8.41}$$

note that eq. (8.40) implies

$$\frac{\mathrm{d}S(\omega_f)}{\mathrm{d}\alpha} = f(\alpha)\,\mathrm{Tr}\left(\frac{\mathrm{d}\omega_f(\alpha)}{\mathrm{d}\alpha}H(\alpha)\right) = 0. \tag{8.42}$$

Taking the equality at the r.h.s., one sees that the state $\omega_f(\alpha)$ fulfils condition (8.34) and hence, $\omega_f(\alpha) = \omega(\alpha)$ and in turn, $S(\omega(0)) = S(\omega(\alpha))$. In other words, any function $f(\alpha)$ that –playing the role of the inverse temperature $\beta(\alpha)$—keeps the entropy constant, will also fulfill the energy conservation condition given by (8.34), so that $f(\alpha) = \beta(\alpha)$. This result can be used to answer in many situations whether a quasi-static process with constant entropy between two Hamiltonians is possible.

8.4.5. Entropy production and reversibility

Leaving aside pathological cases, so far we have shown that entropy in our effective descriptions in terms of equilibrium states can only increase, and remains constant if the protocol is quasi-static. Let us now connect entropy production to reversibility of processes. First, note that for the GGE equilibration model (similarly for the Gibbs model since it is a particular case of the former), condition (8.34) is invariant if one reverses the process. More specifically, given $H(\alpha)$ and $\omega_{\mathrm{GGE}}(0)$ as initial state, condition (8.34) determines the trajectory of states $\omega_{\mathrm{GGE}}(u)$, with u from 0 to 1. Now, we can consider the trajectory $H(\tilde{\alpha})$ with initial state $\omega_{\mathrm{GGE}}(\tilde{\alpha} = 0)$ with $\tilde{\alpha} = 1 - \alpha$. One can easily verify that

$$\mathrm{Tr}\left(\frac{\mathrm{d}\omega_{\mathrm{GGE}}(\tilde{\alpha})}{\mathrm{d}\tilde{\alpha}} Q_j(\tilde{\alpha})\right) = 0, \quad \forall j = 1, \ldots, m. \tag{8.43}$$

Hence, the equilibrium state for the trajectory $H(\tilde{\alpha})$ is given exactly by $\omega_{\mathrm{GGE}}(\tilde{\alpha} = 1 - \alpha)$ and thus, the protocol is reversible. In other words, we have seen that for the GGE equilibration model reversible protocols correspond to arbitrarily slow protocols where no entropy is produced on the *system and bath* together, exactly as is the case for phenomenological thermodynamics.

An important consequence of phenomenological thermodynamics is that reversible transformations are always beneficial in thermodynamic protocols, a phenomenon which is referred to as the *minimum work principle*. We will later see that this principle naturally holds when the model of equilibration is given by Gibbs states, but its range of applicability is considerably reduced when the equilibrium states are described by GGE.

Before we go on to discuss explicit work extraction protocols, let us stress that the entropy in SB, which can only increase or remain constant, is not simply the sum of the entropies of S and B. This happens because we are considering interacting quantum systems that show correlations between S and B. This is true both in the exact and the effective description. Indeed, in general the von Neumann entropy in SB is smaller than or equal to the sum of local entropies

$$S(\rho^{(i)}) \leq S(\rho_S^{(i)}) + S(\rho_B^{(i)}), \tag{8.44}$$

with equality if and only if $\rho^{(i)} = \rho_S^{(i)} \otimes \rho_B^{(i)}$, i.e., when S and B are completely uncorrelated. Thus, entropy-production in our set-up does not always mean that entropy is *locally* produced in the system and the bath. The generation of entropy is not always associated with the generation of correlations, as in Ref. (ELV10), but rather to the mixing induced by equilibration processes.

8.5. Work extraction with Gibbs ensembles

8.5.1. Setting of work extraction

We now turn to presenting bounds and optimal protocols for work extraction for the case of equilibration to the Gibbs ensemble given by $\omega_{\text{Gibbs}}(\rho, H)$. In the case of Gibbs thermalization, analytic bounds have already been obtained within a set of operations similar to the one considered here, but with some crucial differences. This is the case, for instance, in Refs. (Ali79; AHHH04; AN05b; EVdB11; Abe13; AG13). There, it is assumed that the system equilibrates, upon contact with the bath, as,

$$\rho^{(i)} \mapsto \rho^{(i+1)} := \omega_\beta(H^{(i+1)}) = \frac{e^{-\beta H^{(i+1)}}}{Z}, \tag{8.45}$$

where $\beta > 0$ is assumed to be *fixed* throughout all the protocol. In contrast, in the model that we will consider, given by $\omega_{\text{Gibbs}}(\rho, H)$ in (8.4), the inverse temperature $\beta > 0$ is defined so that the average energy is preserved in each process of equilibration. Hence, in general it will not remain constant throughout the protocol. Nevertheless, these two models of equilibration are related so that (8.45) can be seen as a particular case of (8.4). Suppose that the total energy of SB will not be substantially affected by the energy pumped or subtracted in all the quenches $H^{(i)} \mapsto H^{(i+1)}$. In this case, the parameter β will remain almost constant, since $\omega_{\text{Gibbs}}(\rho^{(i)}, H^{(i+1)}) \approx \omega_\beta(H^{(i+1)})$; that is, the two models coincide. This is expected to take place is in the limit of an infinite bath B. Hence, our formalism and the following bounds can be regarded as a correction to the usual results, due to the fact that the bath is not infinite and loses energy and degrades in each of the equilibrations that it induces on S.

In order to study the work extraction problem, we focus first on the *minimal work principle*, which is intimately related to the work extraction problem and other tasks in thermodynamics such as the erasure of information (Landauer's

Principle). Analogously to the work extraction problem, the minimal work principle has been studied within the model of equilibration (8.45) (see (AN05b) and references therein). Here, we extend these results under the model of equilibration (8.4).

8.5.2. Minimal work principle

The minimal work principle states that, given an initial equilibrium state and a given process, the work performed on the system is minimal for the slowest realisation of the process (AN05b). Here, as we generically take the convention that work is *extracted* from the system, minimising the work cost corresponds to maximising W in (8.26).

Let us consider an initial state $\rho^{(0)}$ and a protocol that changes the Hamiltonian from $H^{(0)}$ to $H^{(f)}$ according to a certain trajectory $t \mapsto H(t)$. The velocity of the protocol is determined by the number of quenches N and the total work performed is given by the sum of the individual work $W^{(i)}$ in the i-th step,

$$\begin{aligned} W &= \sum_{i=0}^{N-1} W^{(i)} = \sum_{i=0}^{N-1} \mathrm{Tr}\left(\rho^{(i)}(H^{(i)} - H^{(i+1)})\right) \\ &= \mathrm{Tr}\left(\rho^{(0)} H^{(0)}\right) - \mathrm{Tr}\left(\rho^{(N)} H^{(N)}\right) \\ &+ \sum_{i=1}^{N-1} \mathrm{Tr}\left((\rho^{(i)} - \rho^{(i+1)}) H^{(i+1)}\right), \end{aligned} \tag{8.46}$$

where $H^{(N)} = H^{(f)}$ and in eq. (8.46) we have simply reorganised the terms and added and subtracted the quantity $\mathrm{Tr}(\rho^{(N)} H^{(f)})$. We can now use our model of equilibration

$$\rho^{(i)} = \omega_{\mathrm{Gibbs}}(\rho^{(i-1)}, H^{(i)}) = \frac{e^{-\beta^{(i)} H^{(i)}}}{Z^{(i)}} \tag{8.47}$$

for all $i \geq 1$, where $Z^{(i)} = \mathrm{Tr}(e^{-\beta^{(i)} H^{(i)}})$ and $\beta^{(i)} > 0$ is determined by the conservation of average energy: $\mathrm{Tr}(\rho^{(i-1)} H^{(i)}) = \mathrm{Tr}(\rho^{(i)} H^{(i)})$. One can easily check that energy conservation implies that the last sum in (8.46) vanishes, which implies that

$$W = \mathrm{Tr}\left(\rho^{(0)} H^{(0)}\right) - \mathrm{Tr}\left(\rho^{(N)} H^{(f)}\right), \tag{8.48}$$

where $\rho^{(N)}$ depends on the protocol. Note that this calculation is valid without assuming that $\rho^{(0)}$ is an equilibrium state.

From eq. (8.48) we see that given a fixed final Hamiltonian $H^{(f)}$, the protocol that costs the minimum amount of work (and maximises the extracted work W) is given by the one that leaves the final state with the least average energy. Since the average energy is monotonic with the entropy for Gibbs states of positive temperature, we conclude that the optimal protocol is the one minimising the entropy of the final state $\omega^{(N)}_{\text{Gibbs}}$. Furthermore, as the entropy can only increase throughout the protocol (see Sec. 8.4), a protocol creating no entropy is optimal.

It has to be stressed that this holds true only as long as the final temperature of the Gibbs state is positive, which happens if

$$\operatorname{Tr}(\rho^{(N)}H^{(f)}) \leq \frac{1}{d}\operatorname{Tr}(H^{(f)}). \tag{8.49}$$

From the results in Sec. 8.4 (see Example 1) it is clear that this is true if the initial state $\rho^{(0)}$ is a Gibbs state with positive temperature and the degeneracy of the ground state of the Hamiltonians along the trajectory $H(t)$ remains constant. We thus conclude that the minimal work-principle holds in the effective description by Gibbs states for trajectories of generic local Hamiltonians, which have non-degenerate ground spaces for typical choices of the Hamiltonian parameters (AL81).

8.6. Work extraction with time averaged states

8.6.1. Minimal work principle

In this section we discuss the minimal work principle to the situation when the equilibration model is the time averaged state. Due to the absence of a one to one relation between energy and entropy for TA states, we expect that the minimal work principle will not be satisfied in general for initial TA states. Yet, in this section we identify some scenarios where the principle remains valid. Our results complement those of Ref. (AN05b), where the applicability of the minimal work principle was studied for initial Gibbs states and the framework of unitary evolutions under time-dependent Hamiltonians.

As an initial state we take an arbitrary equilibrium state which takes the form $\omega^{(1)} = \sum_k^{(i)} p_k^{(1)} P_k^{(1)}$. Similarly, any state during the process reads

$$\omega^{(i+1)} = \sum_k^{(i)} P_k^{(i+1)} \omega^{(i)} P_k^{(i+1)} \tag{8.50}$$

for $i \geq 0$, where

$$H^{(i)} = \sum_k E_k^{(i)} P_k^{(i)} \tag{8.51}$$

with $P_k^{(i)}$ being the projectors onto the corresponding eigenspaces. The total work of an arbitrary process of N steps is given by

$$W = \operatorname{Tr}\left(H^{(1)}\omega^{(1)}\right) - \operatorname{Tr}\left(H^{(f)}\omega^{(N)}\right). \tag{8.52}$$

Let us now make use of the fact that the time-average $\omega^{(i+1)}$ can be written as a finite mixture of unitaries $\omega^{(i+1)} = T^{(i+1)}(\omega^{(i)})$, with $T^{(i)}(\cdot) = \sum_k q_k^{(i)} U_k^{(i)} \cdot U_k^{(i)\,\dagger}$. Since the composition of any number of mixtures of unitaries is again a mixture of unitaries, we see that the final state $\omega^{(N)}$ is related to the initial state $\omega^{(1)}$ by such a mixture of unitaries,

$$\begin{aligned} \operatorname{Tr}\left(H^{(f)}\omega^{(N)}\right) &= \operatorname{Tr}\left(H^{(f)} \sum_k q_k U_k \omega^{(1)} U_k^{\dagger}\right) && (8.53)\\ &\geq \min_U \operatorname{Tr}(H^{(f)} U \omega^{(1)} U^{\dagger}), && (8.54) \end{aligned}$$

where q_k and U_k are the probabilities and the unitaries of the total mixture of unitaries. Now we can use that the unitary that minimises the lower bound in eq. (8.54) is the one that transforms the state in a passive state, i.e.,

$$\operatorname{argmin}_U \operatorname{Tr}(H^{(f)} U \omega^{(1)} U^{\dagger}) = \sum_k (\omega^{(1)})^{\downarrow}_k E_k^{(f)}, \tag{8.55}$$

where $(\omega^{(1)})^{\downarrow}$ is the vector of eigenvalues of $\omega^{(1)}$, ordered such that $(\omega^{(1)})^{\downarrow}_k \geq (\omega^{(1)})^{\downarrow}_l$ if $E_k^{(f)} \leq E_l^{(f)}$.

While the above results set a limit to arbitrary processes, the minimal work principle is formulated for a fixed process, i.e., a well defined path in Hamiltonian space. If the initial state together with the Hamiltonian path are such that the final states (i.e., the family of states produced at different speeds of the protocol) are passive, our considerations above show that the slowest realisation of the process is the optimal one. However, for those trajectories that bring the system into a non-passive state, the minimal work principle is not guaranteed to hold. In fact, in Ref. (AN05b) it is shown that for initial Gibbs states and unitary processes the applicability of the minimal work principle is restricted to trajectories with no level-crossings. It is easy to see that such trajectories are precisely those that preserve the passivity of the initial state.

8.7. Work extraction with generalised Gibbs ensembles

Let us now consider the general case of GGE models of equilibration. Similarly to the previous Sec. (8.6), we cannot provide a general answer for the relation between enetropy production and the minimal work priniple, which is to be expected, since -unlike for Gibbs states- there is not a clear correspondence between energy and entropy in GGE states.

Here we will focus on a particular class of physical systems described by free fermions, the equilibrium states of which are well described by the Generalised Gibbs Ensemble. This is enough to reveal important differences in the minimal work principle for Gibbs and GGE states.

Besides studying the minimal work principle beyond Gibbs ensembles, there are important reasons for largely focusing on quadratic fermionic models, namely:

1. They can be efficiently simulated, allowing us to test how well the effective description of the system approximates its real (exact) dynamics.
2. They are integrable, which implies that a GGE description is in general necessary to capture their equilibration behaviour (PSSV11; GE15).
3. They can be simulated with ultra-cold atoms in optical lattices in and out of equilibrium (LSA$^+$07).

While the discussion presented here is focused on fermionic systems, it should be clear that their bosonic lattice instances (BDN12; BDZ08) and even bosonic continuous systems (LEG$^+$15; SFL$^+$15) can be captured in an analogous framework with very similar predictions. The latter situation is specifically interesting as modelling the physics of ultra-cold atoms on atom chips that is expected to provide an experimental platform probing the situation explored here where a GGE description is relevant.

8.7.1. Free fermionic systems

We consider quadratic fermionic Hamiltonians of the form

$$H = \sum_{i,j=1}^{n} c_{i,j} a_i^\dagger a_j, \tag{8.56}$$

where n is the number of different modes and the fermionic operators satisfy the anti-commutation relations $\{a_i, a_i^\dagger\} = \delta_{i,j}$, $\{a_i, a_j\} = \{a_i^\dagger, a_j^\dagger\} = 0$. The Hamiltonian H can be transformed into

$$H = \sum_{k=1}^{n} \epsilon_k \eta_k^\dagger \eta_k \tag{8.57}$$

making use of mode transformations unitarily transforming one vector of fermionic operators to a new one. It is well known that equilibrium states of Hamiltonians of the form (8.57) are not well described by Gibbs states, but rather by generalised Gibbs ensembles (GGE), with the conserved quantities being the energy modes $Q_k = \eta_k^\dagger \eta_k$, $k = 1, \ldots, n$ (GE15). Notice that the number of conserved quantities is equal to the number of distinct modes n and hence linear and not exponential in the system size. We define the correlation matrix $\gamma(\rho)$ of a state ρ as the symmetric matrix having entries

$$\gamma_{i,j}(\rho) = \mathrm{Tr}(\eta_i^\dagger \eta_j \rho). \tag{8.58}$$

If the state ρ is Gaussian, then $\gamma(\rho)$ contains all information about ρ, as well as its time evolution under Hamiltonians of the type (8.57). That means that the full density matrix ρ can be reconstructed from just knowing the correlation matrix. The correlation matrix of the GGE $\omega_{\mathrm{GGE}}(\rho, H, \{\eta_k^\dagger \eta_k\})$ is found by maximising the entropy while preserving all $Q_k = \eta_k^\dagger \eta_k$, which simply reduces to dephasing the correlation matrix defined in (8.58) to the diagonal (see Appendix A.5 for details). This provides a simple method for obtaining $\gamma(\omega_{\mathrm{GGE}}(\rho, H, \{\eta_k^\dagger \eta_k\}))$.

Most importantly, these GGE descriptions are also Gaussian states, and hence also fully described by their correlation matrix. In particular, any such GGE state ω_{GGE} is described completely by the n numbers $\mathrm{Tr}(\omega_{\mathrm{GGE}} \eta_i^\dagger \eta_i)$, $i = 1, \ldots, n$. Furthermore, it also only depends on the second moments, i.e., the correlation matrix, of the initial state from which it was constructed. Hence, in the following we can always restrict to Gaussian states, even if the initial state is not Gaussian: All the results are unchanged if we replace the initial state with a Gaussian state that has the same correlation matrix.

Consequently, in the following, we can reduce the discussion to the level of correlation matrices instead of the full density matrices. This allows us to perform numerical simulations of the real time-evolution as well as the effective description of large systems, because they have dimension $n \times n$ instead of $2^n \times 2^n$ as needed to describe the full density matrix.

8.7.2. Optimal protocols for work extraction and minimal work principle for free fermions

In this Sec. we derive analogous results of those obtained in Sec. 8.6.1, but in terms of the correlations matrix instead of the full density matrix. More concretely, we will show that, while the minimal work principle does not hold in general for free ferminonic equilibrium states, we can identify some situations where it remains valid.

Analogously to previous sections, we start with a GGE state and consider a sequence of Hamiltonian transformations, from $H^{(0)}$ to $H^{(f)}$. In this case, we consider transformations to any quadratic Hamiltonian of the form (8.57). The final energy of a realization with N steps is given by,

$$\operatorname{Tr}\left(H^{(f)}\omega_{\mathrm{GGE}}^{(N)}\right) = \sum_k p_k^{(N)}\epsilon_k^{(f)}. \tag{8.59}$$

As we show in Appendix A.6, it satisfies $\operatorname{Tr}(\omega_{\mathrm{GGE}}^{(N)}H^{(f)}) = \sum_k n_k^{(N)}\epsilon_k^{(f)}$, where

$$\operatorname{Tr}(\omega_{\mathrm{GGE}}^{*}H^{(0)}) = \sum_{k=1}^{n}(d^{(0)})_k^{\downarrow}(\epsilon^{(0)})_k^{\uparrow}, \tag{8.60}$$

where $d_k^{(0)}$ are the eigenvalues of $\gamma(\rho^{(0)})$ and the symbols $^\uparrow$ and $^\downarrow$ indicate that the lists are ordered in increasing and decreasing order, respectively. An explicit protocol saturating this bound is constructed in A.6. The optimal protocol is found to be *reversible*, so that no entropy is generated, and one needs to perform an arbitrarily large amount of quenches to reach optimality.

In the optimal final state, $\omega_{\mathrm{GGE}}^{*}$, the diagonal elements of the correlation matrix, corresponding to the population of the energy modes, decay as the energy of the modes increases. This form is reminiscent of the passive states previously introduced. However, in general, states of the form $\omega_{\mathrm{GGE}}^{*}$ do not need to be passive: While in passive states the occupation probabilities of the global energy eigenstates are decreasing with increasing energy, here only the occupation probabilities of different fermionic *modes* decreases with increasing energy of the mode. The total energies are however obtained by combinations of different modes. An example for a state that is non-passive, but where the mode-populations are decreasing with increasing mode-energy is provided in Appendix A.6.

Regarding the minimal work principle, one can use a similar line of reasoning as in Sec. 8.6.1. For a fixed process, the minimal work principle is guaranteed to hold true as long as the possible final states—which are realised by implementing the process at different speeds—have the form (8.60), i.e., their populations decrease with the energy of the modes. If this condition is not satisfied, the minimal work principle does not hold in general.

8.8. Numerical results: comparison between exact dynamics and effective descriptions

In this section we compute the work extracted in different scenarios by (i) a numerical simulation of the exact unitary evolution of the system, (ii) using the effective description in terms of Gibbs states, and (iii) in terms of GGE states. As a physical system, we consider a chain of fermions, taking as an initial Hamiltonian,

$$H^{(0)} = \sum_{i=1}^{n} \epsilon_i a_i^\dagger a_i + \sum_{i=1}^{n-1} g \left(a_i^\dagger a_{i+1} + a_{i+1}^\dagger a_i \right) . \tag{8.61}$$

We discuss both global transformations of the Hamiltonian, as in Sec. 8.7.2, and local ones. In all cases we find a very good agreement between the real dynamics and the GGE effective description.

Besides comparing the effective descriptions with the real dynamics, in this section we also study the applicability of the minimal work principle. We give an explicit example of a process in which producing entropy is beneficial for work extraction, thus apparently violating the minimal work principle. This apparent violation can be explained because: (i) the equilibrium states of the process are not well described by Gibbs states, but rather by GGE states, and (ii) the conditions for the applicability of the minimal work principle for GGE states discussed in Sec. 8.7.2 are not satisfied.

8.8.1. Work extraction with unrestricted Hamiltonians and free fermions

Here, we take as the initial state $\rho^{(0)}$ a GGE state whose populations $\gamma_{ii} \in (0,1)$ in (8.58) are chosen i.i.d. from a Gaussian distribution. We then apply the protocol described in Appendix A.6 for maximal work extraction, and compare the results obtained by the exact dynamics and the GGE model of equilibration. The exact dynamics are computed by, after the the ith quench, letting the system unitarily evolve under the Hamiltonian $H^{(i)}$ for a time much longer than the time scale of equilibration. Fig. 8.2 shows the results obtained using both approaches. It shows a very good agreement, as long as the number of fermions is sufficiently large (in the figure $n = 100$). Yet small discrepancies are observed, which is due to the fact that we implement global quenches, for which the state may not equilibrate. Note that, when performing local quenches and starting with a Gibbs state, as in Fig. 8.3, equilibration of local observables is guaranteed and the agreement is excellent.

We can also see in Fig. 8.2 how work increases as the process becomes slower, becoming maximal in the limit $N \to \infty$, when reversibility is achieved. This is nothing but a realisation of the minimal work principle. Indeed, the principle can be applied in this case for a twofold reason: First, the exact dynamics are well described by GGE states. Second, the final states of the applied protocol

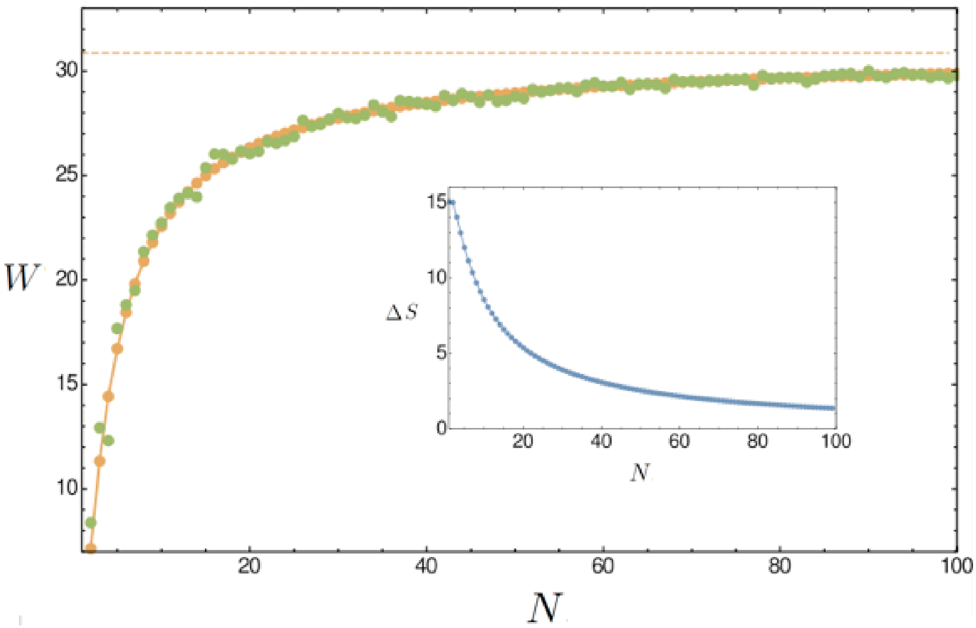

Figure 8.2.: Extracted work in the optimal protocol with unrestricted Hamiltonians. As an initial state, we take a diagonal state in the basis $H^{(0)}$, with the populations $\{p_k^{(0)}\}$ chosen at random between 0 and 1. We take $\epsilon = 1, g = 0.8$ and $N = 100$. In order to simulate the real dynamics, after every quench, we let the system evolve for a time chosen at random between $20/g$ and $100/g$. In green, we show the results using the actual unitary dynamics, in yellow our effective description in terms of GGE states, and in dashed lines the analytical result leading to eq. (8.60). The inset figure shows the entropy generated in the effective description using GGE states.

are passive (or, more precisely, are of the form (8.60)), which is a sufficient condition for the applicability of the principle when dealing with free fermions, as discussed in Sec. 8.7.2.

8.8.2. Work extraction with restricted free fermionic Hamiltonians with a Gibbs initial state

Let us now assume that the Hamiltonian can only be locally modified, as discussed in Sec. 8.3. The Hamiltonian (8.61) is split in three components.

$$H_S = \epsilon_1 a_1^\dagger a_1 \tag{8.62}$$

(i.e., S is a single fermion),

$$V = g(a_1^\dagger a_2 + a_2^\dagger a_1) \tag{8.63}$$

and $H_B = H^{(0)} - V - H_S$, with $H^{(0)}$ given in (8.61). Our capability to change the Hamiltonian is thus reduced to a single parameter: the local energy ϵ_1. Note that the coupling between the S and the B is not assumed to be weak. The initial state takes the form,

$$\rho^{(0)} = \rho_S \otimes \frac{e^{-\beta H}}{\mathcal{Z}}, \tag{8.64}$$

where ρ_S is initially out of thermal equilibrium. For example, in Fig. 8.3, it is set to a lower temperature than the bath.

Fig. 8.3 shows the extracted work from ρ_S as a function of the number of quenches N, which is computed using the real exact unitary evolution, and the effective description in terms of both GGE and Gibbs states. The agreement between the unitary dynamics and the GGE description is excellent, for any value of N and the parameters, but the Gibbs states fail to describe the process. Even if the bath is initially in a Gibbs state, see eq. (8.64), the posterior evolution of SB can not be correctly described by them. Although the description with in terms of Gibbs ensembles is quantitatively incorrect, it is fair to say that it describes some qualitative features of the results. In particular, the exact dynamics satisfies the minimal work principle, and so does the effective description with Gibbs states. This follows because condition (8.49) is satisfied during the process. However, as we show in the next section, condition (8.49) can fail to predict the applicability of the minimal work principle.

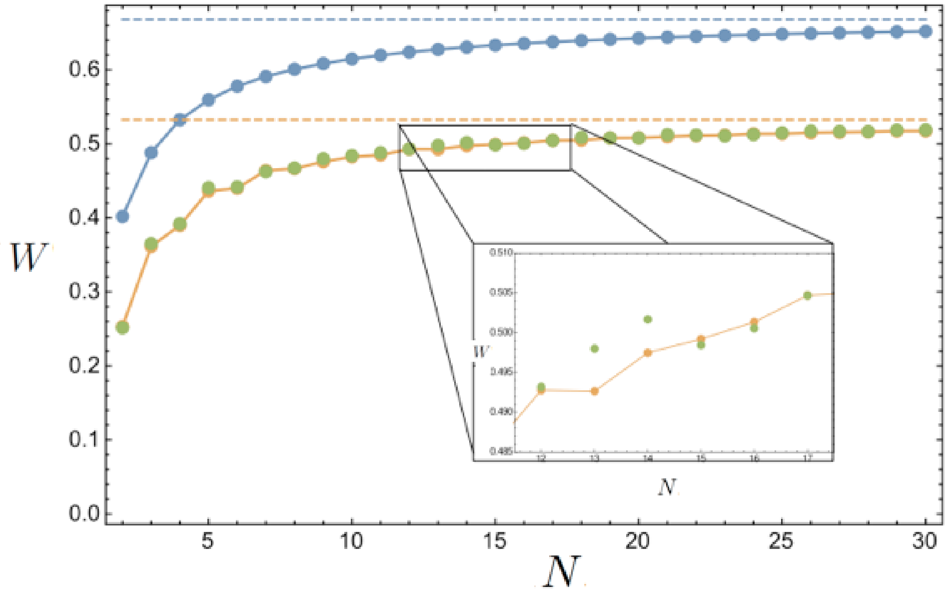

Figure 8.3.: Extracted work with only local transformations on the state of the system. The different points correspond to the exact unitary evolution (in green), to the effective evolution in terms GGE states (in yellow), and the effective evolution using Gibbs states (in blue). The continuous lines correspond to transformations with $N \to \infty$. As an initial state we take, $\beta = 1/2$, $\mathrm{Tr}(a_1^\dagger a_1 \rho_S) = 0.1$, $n = 100$. For the initial Hamiltonian, $\epsilon_0 = 0.1$, $\epsilon_i = 1$ $\forall i \neq 1$, $g = 0.5$. As a protocol we perform a first quench to $\epsilon_1 = 4.3$, followed by $N - 1$ equidistant quenches back to the original Hamiltonian. As in Fig. 8.2, the exact evolution is obtained by letting system and bath interact for a time much larger than the equilibration time ($t_{\mathrm{Eq}} \propto 1/g$).

8.8.3. Work extraction with free fermionic restricted Hamiltonians with a GGE initial state

Equilibrium states when dealing with Hamiltonians of the type (8.57) are well described by GGE states, it is therefore natural to generalise the initial state (8.64) to,

$$\rho_0 = \rho_S \otimes \omega^{(B)}_{\mathrm{GGE}} \tag{8.65}$$

where ω_{GGE} is a GGE state with respect to the local Hamiltonian of B, $H_B = \sum_{k=1}^{n} \epsilon_k^{(B)} \eta_k^{(B)\dagger} \eta_k^{(B)}$. Let us now pick a very particular initial state given by

$$\mathrm{Tr}(\omega^{(B)}_{\mathrm{GGE}} \eta_k^{(B)\dagger} \eta_k^{(B)}) = \begin{cases} 1 & k \geq K \\ 0 & k < K \end{cases} ,$$

for some $K < n$. That is, only the K most energetic modes are populated. No actual thermal state with positive temperature would have such properties due to the population inversion of the fermionic modes. It is important to acknowledge, however, that if we would chose an effective description as a Gibbs state for such initial states, we would nevertheless obtain a positive effective temperature provided that condition (8.49) is satisfied. This will be the case as long as the number of populated energy-levels K is small enough. Indeed, for any finite K, but large n, the energy-density in the state is much lower than the critical energy-density needed for negative effective temperatures.

The work extracted in a particular protocol with initial state (8.65) is plot in Fig. 8.4. The results clearly show how the extracted work decreases with the time spent in the process. Therefore, more work is extracted when more entropy is produced, and the minimal work principle does not apply in this situation. In fact, this is to be expected because both the initial and the final state of the protocol are highly non-passive, and thus the conditions described in Sec. 8.7.2 are not satisfied. However, when using an effective description in terms Gibbs states, we would have predicted that it is always beneficial to use a quasi-static, reversible protocol since condition (8.49) is satisfied for the case described in Fig. 8.4.

8.9. Concluding remarks

In this chapter, we have brought together the fields of research on equilibration and quantum heat engines. Our main contribution is to go beyond the usual paradigm of thermodynamics where work is extracted from a system in weak thermal contact with an infinite heat bath at a given fixed temperature. Instead, we consider closed quantum many-body systems of finite size and with

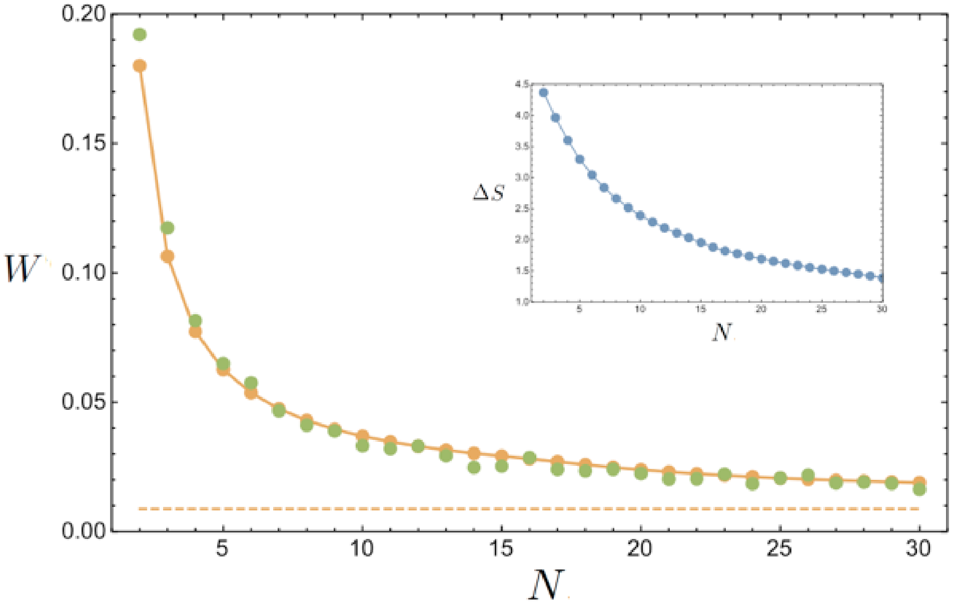

Figure 8.4.: The extracted work achieved with only local transformations on the state of the system. As an initial state we take the one specified by $K = 32$, $\mathrm{Tr}(a_1^\dagger a_1 \rho_S) = 0.1$, and $n = 150$. For the initial Hamiltonian, we take $\epsilon_0 = 0.1$, $\epsilon_i = 1 \ \forall i \neq 1$, $g = 0.5$. As a protocol we perform a first quench to $\epsilon_1 = 1.6$, followed by $N - 1$ equidistant quenches back to the original Hamiltonian. The different points correspond to the exact unitary evolution (in green), to the effective evolution in terms GGE states (in yellow), and to infinitesimally slow protocol ($N \to \infty$). As in 8.2, the real evolution is obtained by letting system and bath interact for a sufficiently long time (chosen at random).

strong coupling between its constituents. We make use of recent insights into the study of states out of equilibrium: closed many body systems do not equilibrate, but can be effectively described as if they had equilibrated when looking at a restricted, although most relevant, class of observables. The effective equilibrium state that describes the system for these observables is, however, not necessarily given by a Gibbs state; and even if so, its temperature will not remain constant. In this case the effective equilibrium state is given by the time averaged state, the GGE or the Gibbs state, depending on the particular kind of system considered, as well as the family of observables that are taken into account.

With this in mind, we have put forward a framework that studies work extraction of closed many body systems, incorporating Hamiltonian quenches as well as equilibrations according to the three models mentioned before. We do not only assume that effective equilibrium state is a good description of the state evolving after a single quench, but also that such an equilibrium state can be taken as the initial state to describe further evolutions under subsequent quenches. This model, which is successfully tested for free fermions, is what allows us to describe a closed system similarly to the way open systems (in contact with baths) are described in thermodynamics. Thus, we can formulate similar questions regarding work and entropy production and indeed recover many of the phenomena present for open systems.

In particular, we provide stringent conditions for the absence of entropy production in quasi-static protocols. This turns to be intimately related to the optimal protocols for work extraction and the minimal work principle, which roughly speaking states that the work performed on the system is minimal for the slowest realisation of a given process. We find that the minimum-work principle can break down in the presence of a large number of conserved quantities, while it remains intact if system and bath together can be well described by a Gibbs ensemble, even in the strongly interacting regime. This is shown numerically with the paradigmatic example of free fermions for which the extracted work decreases with the time spent in the process if we consider the GGE as equilibration model, but the minimal work principle still applies when the Gibbs description is assumed.

9. Conclusions and outlook

This thesis is devoted to the study of thermodynamic processes in the quantum regime. Our work aimed at advancing our understanding of the implications that quantum phenomena, such as coherence and entanglement, have for thermodynamic processes. Conversely, we have also investigated the limitations that thermodynamic environments have on quantum information processing. Our results provide new insights and quantitative results in the interplay of quantum physics and thermodynamics, which naturally raise open questions and challenges. In this last chapter we review the main conclusions of each chapter and explore open directions and future work.

Work extraction from quantum systems

In Chapter 3, we have studied work extraction in the quantum regime. Building on the seminal work by (PW78; Len78), we have studied the phenomena of activation of passive states. We have explored the role of entanglement in this process, by constructing different protocols which suggest that entanglement is directly related to the velocity of the work extraction process: the faster it is (i.e., more power), the more entanglement one needs to create. These results are in agreement with Ref. (GLM03), where entanglement was linked to the speed of unitary evolutions. Natural open questions include obtaining a direct quantitative relation among entanglement and power in energy exchanges among multipartite systems (see the work of (BVMG15) in that direction), and also to study the role of entanglement in other thermodynamic processes such as heat exchange.

In a related project, we have bounded the amount of work that can be obtained from activation processes. This naturally renders the family of the *most energetic passive states* (MEPS), which is the dual of the Gibbs states, which are the least energetic passive states. Because of this duality, we have shown that the MEPS provide fundamental bounds on the work that can be extracted from a quantum system which only depends on its entropy and energy. For future work, it would be interesting to study the role of MEPS in the scenario discussed in Chapter 4, where work is extracted from the system using an auxiliary thermal bath, in order to connect our considerations to recent relevant results obtained in this setting (EVdB11; BaHO$^+$13; RW14; Abe13; AG13; SSP14; WGE14).

Second law of thermodynamics

In Chapter 4, we have studied a possible generalisation of the second law in out of equilibrium processes, following the works of Refs. (EVdB11; RW14). By considering a system together with a thermal state, possibly of finite size, we have constructed an exact equality which holds for arbitrary unitary operations on them. The second law naturally follows from such an equality. This formulation, developed in Refs. (EVdB11; RW14), allowed us to obtain corrections to the second law from the finite size or the structure of the thermal bath.

An interesting open question is to find what is the optimal work extraction protocol given a bath of finite size. In particular, the optimal protocol discussed in 4.3 approaches the bound given by the second law with a correcting term that decreases linearly with the size of the bath, whereas the finite size corrections in Sec. 4.4 can be shown to decrease quadratically by using the results of (RW14). These two results provide lower and upper bounds to the fundamental finite size corrections of the second law, and finding tighter bounds is desired.

Furthermore, we have shown that for a bath of identical two level systems, the second law can not be saturated, even if the bath has infinite size. This result relies on the presence of energy gaps in the bath spectrum. However, in the presence of very weak interactions, such energy gaps could practically disappear, although many other properties of the bath spectrum would be preserved. Understanding the implications of weak interactions in the bath Hamiltonian for our results is hence desired. In particular, one would like to understand whether a small interaction between the bath constituents can significantly change the limitations developed in Sec. 4.5.

Quantum fluctuations of work

In chapter 5 we have explored the possibility of describing the fluctuations of work in coherent processes. Taking as a starting point the measurement scheme for characterizing fluctuations developed in (TLH07), we have explored new measurement schemes that can meaningfully describe processes for states with quantum coherence. First we have proven a no-go result: There is no measurement scheme to estimate the fluctuations of work that can be in agreement simultaneously with (i) the classical fluctuation theorems (i.e., the results of (TLH07)) and (ii) the first law of thermodynamics for states with quantum coherence. This result provides a fundamental limitation on the possibility of measuring the fluctuations of work in coherent processes. Despite this result, we have constructed a collective measurement scheme, which acts on two copies of the state, that reproduces exactly the results of (TLH07) and at the same time is able to describe a family of quantum coherence processes.

A natural open question is to consider measurements involving more copies in order to obtain better estimation schemes. One would expected that, as more copies of the state are available, measurements schemes with a lower back action can be developed, which could in principle allow for satisfying requirement (ii) with higher and higher level of approximation. However, let us note that we have put a considerable effort on this question, only obtaining partial results. Another very interesting line of research is to develop fluctuation theorems, which are usually formulated for states initially at thermal equilibrium (SPWS08; EHM09; CHT11), in the presence of coherence. Recent results in this direction can be found in (All14; Abe16; AMOP16). Another line of investigation which will be pursued is to connect the results of (Abe16; AMOP16), where the fluctuations of work are defined in an explicit physical system (a weight), with the approach based on quasiprobabilities from (All14; SG15). More concretely, we would like to find a relation between the appearance of negative quasiprobabilities within the framework of (All14; SG15) and the presence of coherence in the weight system within (Abe16; AMOP16).

Extractable work from correlations.

In chapter 6, we have considered a set of correlated states which are thermal at the local level, and hence work can only come from the correlations among them. We have computed the amount of work that can be stored in entangled, separable and correlated states with a fixed entropy, by finding the corresponding optimal states and protocols. These results provide fundamental bounds on the potential of different type of correlations for work storage and extraction.

A technical open question is to extend the optimal protocols derived in Sec. 6.5 beyond qubit systems. Partial results are available in this direction, showing that achieving optimality in some cases is not possible. Another interesting open question is to investigate the scenario in which not only local marginals are thermal, but so are the k-body reduced states (in particular the case of nearest neighbours). This may give an insight into the role of different types of multipartite entanglement in the context of work extraction. Other future directions include understanding the role of correlations in other thermodynamic processes, in this sense Refs. (JR10; Par08) provides an interesting discussion on the consequences of correlations in heat exchanges.

Fundamental limitations for creating correlations in thermodynamic environments

In Chapter 7, we have studied the generation of correlations and entanglement in thermal states at finite temperature. By assuming the possibility of implementing arbitrary unitary operations, we have found fundamental limitations for entanglement generation arising from the finite temperature of the states. Next, we have imposed a constraint on the available energy, which allows us to find the minimal work cost of building correlations and entanglement. These considerations have also been discussed in the presence of a thermal bath, where a simple expression between the work cost and the correlations has been found.

An interesting direction is to understand the complexity required to implement the optimal unitary operations for generating correlations and entanglement. For that, one can use that any unitary operation can be expressed as a combination of elementary gates, which involve at most two body unitary operations. This would also allow us provides us hints on how to construct protocols that are experimentally friendlier. In a similar mindset, finding protocols that generate a substantial amount of entanglement and genuine multipartite entanglement (GME) at high temperatures remains as an important future direction, as this would give a bigger resistance to noise and is important for other applications of GME, such as metrology (TA14).

Finally, from a more theoretical point of view, our results establish a link between fundamental resources of two theories: entanglement theory (HHHH09) and the resource theory of thermodynamics (BaHO^{+}13). Establishing more connections between these two theories is definitely an interesting subject of further research.

Work and entropy production in Generalised Gibbs ensembles (GGE)

In Chapter 8, we have developed a framework to study thermodynamics in closed quantum systems. In particular, we have used one of the most important recent insights from the study of equilibration in quantum systems: Closed many body systems do not equilibrate, but can be effectively described as if they had equilibrated when looking at a restricted, physically relevant, class of observables. Importantly, the corresponding equilibrium state is not necessarily a Gibbs state, but may be very well given by a Generalized Gibbs ensemble (GGE) state. With this in mind, we have studied entropy production and work extraction for such an effective description.

These considerations may help to build connections between two fields of research, quantum heat engines and equilibration in closed systems, that are often disconnected. It is to be expected that many questions will arise in the intersection between both fields. To start with, it would be interesting to test our considerations for bosonic continuous systems, which can be captured in a similar framework that the one used for fermionic systems. Bosonic systems are specially interesting as it can be modelled in ultra cold atoms (LEG$^+$15; SFL$^+$15). In a more theoretical line, we would like to gain a better understanding on how equilibration beyond the weak coupling regime affects the performance of heat engines (see (GRE14; SSLB16) for recent works in this direction).

A. Appendices

A.1. Entanglement quantification

In this appendix we expand the explanations of the used entanglement measure and its lower bounds in more detail. To introduce the mentioned measure, consider an N-partite system in a pure state ψ. We define its entropy vector $\vec{S}$ (HdV13; HPLdV13) as a string, whose elements are the entropies of the reduced states of all subsystems of our N-partite system:

$$S_k(\psi) = \sqrt{2(1 - \mathrm{Tr}(\rho_k^2))}, \;\; k = 1, ..., 2^{N-1} - 1, \tag{A.1}$$

where the index k runs over all possible bipartitions $\Gamma = \{(\gamma_k|\overline{\gamma_k})\}$ of $\{1, 2, ..., N\}$; and ρ_k is the corresponding reduced state: $\rho_k = \mathrm{Tr}_{\overline{\gamma_k}}(|\psi\rangle\langle\psi|)$.

The linear entropy is used in (A.1) for mathematical convenience. Similarly to the standard entropy of entanglement for bipartite pure states, a non-zero (linear) entropy of ρ_k reflects the presence of entanglement. Therefore, each entry of the vector (A.1) detects entanglement in a particular bipartition.

The entropy vector (A.1) also reveals multipartite entanglement properties of the state, in particular the l-separability (HPLdV13). A pure state is l-separable if it can be written as a tensor product of at most l terms, i.e., in the form $\rho_1 \otimes \rho_2 \otimes ... \otimes \rho_k$. Then, it is easy to realize that a l-separable state contains $2^{l-1} - 1$ bipartitions where the state is separable. Therefore, if we set the entries of S_k in non-increasing order, (i) if the last $2^{l-1} - 1$ entries are zero, then the state is l-separable. In particular, (ii) if the first entry is zero, then the state is entangled (i.e., at least (N-1)-separable). Furthermore, (iii) if the last entry is non-zero, i.e. all entries are non-zero, then the state is genuinely multipartite entangled (GME), or 1-separable. Indeed the last entry can be used to measure GME (HRHBE12).

This measure is extended to mixed states ρ via a convex roof construction (HRHBE12; HdV13; HPLdV13):

$$E_k(\rho) \equiv \inf_{\{p_i;|\psi\rangle\}} \sum_i p_i S_k(\psi_i), \;\; k = 1, ..., 2^{N-1} - 1, \tag{A.2}$$

where the infimum is taken over all possible decompositions $\{p_i; |\psi\rangle\}$ of ρ, and S_k are the entries of the entropy vector arranged in non-increasing order. Then, the statements (i), (ii) and (iii) above also hold for E_k (E_k plays the role of S_k in mixed states).

Since the convex roof construction (A.2) requires an optimization over an infinite set and even determining whether a single entry is nonzero is extremely difficult, we have to find a method to reliably calculate lower bounds to these measures. Refs.(HRHBE12; HdV13; HPLdV13) provide lower bounds on all entries of the entropy vector in terms of the matrix elements of the state ρ. For a given set $\mathcal{C}$ of off- diagonal elements of ρ, they read:

$$E_k \geq \Lambda_k(\mathcal{C}) = \frac{1}{\sqrt{|\mathcal{C}|}} \sum_{(\mathbf{i},\mathbf{j})\in\mathcal{C}} \left[|\langle \mathbf{i}|\rho|\mathbf{j}\rangle| - \min_A \sum_{a\in\Gamma_A^k} \sqrt{\langle \mathbf{i}_a|\rho|\mathbf{i}_a\rangle\langle \mathbf{j}_a|\rho|\mathbf{j}_a\rangle} \right], \quad \text{(A.3)}$$

where the index a runs over all bipartitions $\Gamma = \{(\gamma_k|\overline{\gamma_k})\}$ of $\{1, 2, ..., N\}$ of the set $\{1, ..., N\}$; A enumerates the set of all k-tuples Γ_A^k of the index a; $|\mathbf{i}_a\rangle$ is obtained from $|\mathbf{i}\rangle = |i_1...i_n\rangle$ by replacing i_k by j_k for all $k \in \gamma_a$ and analogously for $|\mathbf{j}_a\rangle$.

The lower bounds (A.3) easily apply to the considered processes in this work. Indeed, given the initial global diagonal state Ω, consider the exchange of populations $P_\mathbf{i}$, $P_\mathbf{j}$ of the states $|\mathbf{i}\rangle$, $|\mathbf{j}\rangle$ respectively; under some unitary process given by:

$$U^{\mathbf{ij}}(t) = \sum_{\mathbf{k}\neq\mathbf{i},\mathbf{j}} |\mathbf{k}\rangle\langle\mathbf{k}| + u^{\mathbf{ij}}(t), \quad \text{(A.4)}$$

where $u^{\mathbf{ij}}(t)$ lives in the linear span of $|\mathbf{i}\rangle$ and $|\mathbf{j}\rangle$ and is unitary. The bounds (A.3) yield for $U^{\mathbf{ij}}\Omega U^{\mathbf{ij}\dagger}$:

$$E_k \geq \Lambda_k = 2\left(|P_\mathbf{i} - P_\mathbf{j}| \left|u_{1,1}^{\mathbf{ij}}(t)\right| \cdot \left|u_{1,2}^{\mathbf{ij}}(t)\right| - \min_A \sum_{a\in\Gamma_A^k} \sqrt{P_{\mathbf{i}_a} P_{\mathbf{j}_a}} \right), \quad \text{(A.5)}$$

Notice that the right hand side of (A.5) can be made time-independent by using $\max_t\{|u_{1,1}^{\mathbf{ij}}(t)|\cdot|u_{1,2}^{\mathbf{ij}}(t)|\} = 1/2$ – a consequence of its unitarity. This leads to the desired expression to compute the k-separability of the state under a permutation of diagonal elements.

Finally, note that E_1 in (A.5), i.e. the first entry of the entropy vector, is equivalent to the PPT criterion. Therefore the bound is exact since the dimension of the subspace is $2x2$ and therefore the PPT criterion is a sufficient and necessary condition. Furthermore, the last bound of (A.5), $E_{2^{N-1}-1}$, is also exact as proven in (HRHBE12). Therefore, our detection criteria is exact both for entanglement and genuine N-partite entanglement and it can be used to quantify them.

A.2. Correlations in degenerate subspaces

Consider the total Hamiltonian

$$H = \sum_{i=1}^{n} h_i = \sum_{i=1}^{n_l} E_i \Pi_i, \qquad g_i = \mathrm{Tr}\Pi_i \tag{A.6}$$

where each $h_i = h := \sum_{a=0}^{d-1} \epsilon_a |a\rangle\langle a|$ (with $\epsilon_0 = 0$) has local dimension d, which we assume to be finite. The number of different global energies, n_l is found to be

$$n_l = C_{n+d-1}^{d-1} = \frac{(n+d-1)!}{n!(d-1)!}, \tag{A.7}$$

which corresponds to the number of non-zero eigenvalues of (6.33). In order to find the passive state associated to (6.33), one has to move such eigenvalues to the lowest energy levels. This operation requires knowledge of the spectrum of h_i. Nevertheless, it will suffice for our purposes to move them to a sufficiently degenerated energy. The degeneracy of a global energy $E_i = \sum_j k_j^{(i)} \epsilon_j$ is equal to $C_n^{k_1^{(i)}, k_2^{(i)}, \ldots, k_d^{(i)}}$. The point is then to find the lowest energy, $E_{\min}$, satisfying $C_n^{k_1^{\min}, k_2^{\min}, \ldots, k_d^{\min}} \geq C_{n+d-1}^{d-1}$, so that the work extracted after such a transformation is simply given by

$$W_{\mathrm{deg}} \geq E_{\rho_{\mathrm{deg}}} - E_{\min}. \tag{A.8}$$

Now, notice that for large n

$$\lim_{n\to\infty} \frac{C_{n+d-1}^{d-1}}{C_n^{n-d, k_2', \ldots, k_d'}} = 0, \qquad \sum_{j=2}^{d} k_j' = d \tag{A.9}$$

with $E' = \sum_{a=2}^{d} k_a' \epsilon_a$. Observe that E' is of the order of the energy of one subsystem (for instance, choosing $k_2' = d$ and $k_j' = 0$ for $j > 2$, we obtain $E' = d\epsilon_2$). Therefore we can take $E_{\min} = E'$ obtaining the desired result.

In the case of $d = 2$ the expression for $E_{\min}$ is particularly simple:

$$W_{\min} = \left[1 - C_n^{pn} p^{np} (1-p)^{(1-p)n}\right] E. \tag{A.10}$$

A.3. Protocols using X-states

Given a set of n thermal qubits, $\tau_\beta^{\otimes n}$, in this section we study the limitations for entanglement creation within unitary transformations of the form:

$$\tau_\beta^{\otimes n} \to U\hat{X} \tag{A.11}$$

where in the computational basis $\hat{X}$ takes the form

$$\hat{X} = \begin{pmatrix} a_1 & & & & & & & z_1 \\ & a_2 & & & & & z_2 & \\ & & \cdots & & & \cdots & & \\ & & & a_n & z_n & & & \\ & & & z_n^* & b_n & & & \\ & & \cdots & & & \cdots & & \\ & z_2^* & & & & & b_2 & \\ z_1^* & & & & & & & b_1 \end{pmatrix}, \tag{A.12}$$

with $n = 2^{N-1}$, $|z_i| \leq \sqrt{a_i b_i}$ and $\sum_i (a_i + b_i) = 1$ to ensure that $\hat{X}$ is positive and normalized (see (**?**) for details). A relevant example of an X-like matrix is,

$$\rho = |GHZ\rangle\langle GHZ| + \frac{\mathcal{I}}{2^n} \tag{A.13}$$

where $|GHZ\rangle = \frac{1}{\sqrt{2}}(|0...0\rangle + |1...1\rangle)$. As shown in (**?**), the GME n-qubit states of the form (A.12) can be computed by the genuine multipartite concurrence,

$$C_{GM} = 2\max\{0, |z_i| - w_i\},\ i = 0, 1, ..., n \tag{A.14}$$

where $w_i = \sum_{j \neq i}^{n} \sqrt{a_j b_j}$.

We wish to maximize (A.14) over all U acting on (A.11). The initial state, $\tau_\beta^{\otimes n}$, has no off-diagonals term in the computational basis. It is then advantageous to apply a unitary operation that only generates one off-diagonal term. Indeed, creating off-diagonal terms results into a stochastic transformation of the diagonal terms, thus increasing the w_i term in (A.14) while the $|z_i|$ term depends only on the highest off-diagonal term. On the other hand, given two diagonal elements a_i, b_i of $\tau_\beta^{\otimes n}$, the biggest off-diagonal term that can be generated by a unitary operation is $|a_i - b_i|/2$, which is obtained by a rotation to the corresponding Bell states. Therefore, the optimal protocol can be thought as a combination of:

1. Rotate two diagonal elements to Bell states in order to maximize $|z_i|$ in (A.14).

2. Permute the rest of diagonal elements to minimize w_i in (A.14). This is implemented by setting the elements in decreasing order (in $w_i = \sum_{j \neq i}^{n} \sqrt{a_j b_j}$, having product of biggest with smallest, second biggest with second smallest, etc.).

Step 1 is optimized by acting on the ground state and the most excited state. On the other hand, the thermal state is already ordered to optimize Step 2. The first step leads to $|z_i| = (1 - e^{-n\beta\epsilon})/\mathcal{Z}^n$; and since $a_i b_i = e^{-\beta\epsilon n}$, we obtain that $w_i = (2^n - 2)e^{-\beta\epsilon n/2}/\mathcal{Z}^n$. In the limit of large n, one easily obtains that $k_B T_{GME}/\epsilon \simeq \frac{1}{2\ln(2)}$.

The previous optimization was done in 2 steps (first maximizing z_i and then minimizing w_i). Arguably this is not the optimal approach, as doing a bit worse in step 1 can have a global benefit. While this being true, one can easily convince himself that the differences are of $\mathcal{O}(1/n)$, and thus essentially rotating the ground state with a very excited state and then optimally permuting the rest of diagonal elements, will always lead to $k_B T_{GME}/\epsilon \simeq \frac{1}{2\ln(2)}$. Any other unitary creating X-states from thermal states can not perform better.

A.4. The energy cost and scaling of the W-state protocol

Given an n-qubit thermal state $\Omega = \tau_\beta^{\otimes n}$ we here find the $n \gg 1$ asymptotic behaviour of the maximal temperature T_{GME} that allows to unitarily create genuinely multipartite entanglement (GME) in the ensemble with the W-state protocol and also calculate the energy cost of the protocol. Here $\tau_\beta = diag(p, vp)$, where $p = 1/(1+v)$ and $v = e^{-\beta E}$ is the Boltzmann weight. If the eigenvectors corresponding to the first excited level of the total Hamiltonian are $\{|w_i^{(1)}\rangle\}_{i=1}^n$ and the ones corresponding to the second excited level are $\{|w_a^{(2)}\rangle\}_{a=1}^{n(n-1)/2}$, then the measure we use has the form (**?**)

$$\mathcal{E}[\Omega] = \sum_{i\neq j} |\Omega_{ij}| - 2\sqrt{\Omega_{00}} \sum_a \sqrt{\Omega_{aa}} - (n-2)\sum_i \Omega_{ii} \tag{A.15}$$

where $\Omega_{ij} = \langle w_i^{(1)}|\Omega|w_j^{(1)}\rangle$ and $\Omega_{ab} = \langle w_a^{(2)}|\Omega|w_b^{(2)}\rangle$.

In short, the W-state protocol is the maximization of $\mathcal{E}$ over all such unitary operations that generate non-diagonal elements only in the eigensubspace of the first excited level (which we denote by $\mathcal{W}_1$). These unitaries can be represented as $U\Pi$, where Π is a permutation operation on the initial state and U is a general $n \times n$ unitary living in $\mathcal{W}_1$. As this representation suggests, we divide the optimization procedure in two steps: (i) maximization over Us for a given Π, and (ii) maximization over Πs. After Π acts, the state becomes $\Omega^\Pi = \Pi\rho\Pi$ and its projection on $\mathcal{W}_1$ we denote by ω^Π. Now, the operation U will act only on ω^Π and take it to $\omega' = U\omega^\Pi U^\dagger$ and since U is unitary, the traces of ω' and

ω^{Π} will be the same. Therefore, we can rewrite (A.15) as

$$\mathcal{E}[U\Pi\Omega\Pi U^{\dagger}]=\sum_{i\neq j}|\omega'_{ij}|-2\sqrt{\Omega^{\Pi}_{00}}\sum_{\alpha}\sqrt{\Omega^{\Pi}_{\alpha\alpha}}-(n-2)\sum_{i}\omega^{\Pi}_{ii}. \tag{A.16}$$

This shows that the maximization of $\mathcal{E}$ over U is reduced to the maximization of $\sum_{i\neq j}|\omega'_{ij}|$ over U. To find this maximum, we first observe that due to the unitarity of U, $\mathrm{Tr}\left((\omega')^2\right)=\mathrm{Tr}\left((\omega^{\Pi})^2\right)$; whence,

$$\sum_{i<j}|\omega'_{ij}|^2=\frac{\mathrm{Tr}\left((\omega^{\Pi})^2\right)-\sum_i(\omega'_i)^2}{2}. \tag{A.17}$$

We now relax for the moment the constraint that ω' and ω^{Π} are unitarily connected and only require that $\mathrm{Tr}\,(\omega')=\mathrm{Tr}\left(\omega^{\Pi}\right)\equiv\alpha$ and $\mathrm{Tr}\left((\omega')^2\right)=\mathrm{Tr}\left((\omega^{\Pi})^2\right)\equiv\alpha^2\lambda$. Here we again divide the optimization in two steps: 1) maximize $\sum_{i<j}|\omega'_{ij}|$ with $\sum_{i<j}|\omega'_{ij}|^2$ fixed and 2) maximize the latter. Now we notice that

1) The maximum is reached for $|\omega'_{ij}|=|\omega'_{i'j'}|$ and therefore $\max\sum_{i<j}|\omega'_{ij}|=\sqrt{\frac{n(n-1)}{2}\sum_{i<j}|\omega'_{ij}|^2}$.

2) From (A.17), the maximum for $\sum_{i<j}|\omega'_{ij}|^2$ is reached when $\sum_i(\omega'_i)^2$ is minimal. Since $\sum_i\omega'_i=\alpha$ is fixed, the minimum for $\sum_i(\omega'_i)^2$ is reached when all $\omega'_i=\frac{\alpha}{n}$, i.e., $\max\sum_{i<j}|\omega'_{ij}|^2=\alpha^2\left(\lambda-1/n\right)/2$.

Finally,

$$\max\sum_{i\neq j}|\omega'_{ij}|=\alpha\sqrt{n(n-1)(\lambda-1/n)}, \tag{A.18}$$

and on this maximum, ω' has the following form:

$$\alpha\begin{pmatrix}\frac{1}{n} & e^{\phi_{12}}\sqrt{\frac{\lambda-1/n}{n(n-1)}} & \cdots & e^{\phi_{1n}}\sqrt{\frac{\lambda-1/n}{n(n-1)}}\\ e^{\phi_{21}}\sqrt{\frac{\lambda-1/n}{n(n-1)}} & \frac{1}{n} & \cdots & e^{\phi_{2n}}\sqrt{\frac{\lambda-1/n}{n(n-1)}}\\ & & \vdots & \\ e^{\phi_{N1}}\sqrt{\frac{\lambda-1/n}{n(n-1)}} & e^{\phi_{N2}}\sqrt{\frac{\lambda-1/n}{n(n-1)}} & \cdots & \frac{1}{n}\end{pmatrix} \tag{A.19}$$

Obviously, being obtained in less restrictive conditions, (A.18) upper-bounds the sought $\max_U\sum_{i\neq j}|\omega'_{ij}|$. Nevertheless, one can prove, that for suitably chosen $\{\phi_{ij}\}$ the matrix in (A.19) can always be unitarily reached from ω^{Π}. The proof is slightly more involved and is conducted by first proving the statement for $n = 3$ by explicitly calculating the corresponding phases (only one phase is necessary to adjust there) and then proving the statement by induction for any n.

Now, having done the maximization over U, we turn to finding the Π with largest

$$\mathcal{E}^{\Pi} = \alpha \left(\sqrt{n(n-1)(\lambda - 1/n)} - n + 2 \right) - 2\sqrt{\Omega^{\Pi}_{00}} \sum_{\alpha} \sqrt{\Omega^{\Pi}_{\alpha\alpha}}, \tag{A.20}$$

where we have plugged (A.18) in (A.16). The quantity λ is defined above as the sum of the squares of the normalized elements of ω^{Π}. Therefore, it is never bigger than 1 which implies that in the $n \to \infty$ limit, $\mathcal{E}^{\Pi}$ in (A.20) will be non-negative only if $\lambda \to 1$. On the other hand, choosing a bigger α and smaller elements in the eigensubspace of the second excited level (which we denote by $\mathcal{W}_2$) and on the ground state will also make $\mathcal{E}^{\Pi}$ bigger. To fulfil all this we choose Π so that it takes the smallest element of Ω, $p^n v^n$, to the ground state, the biggest one, p^n, to $\mathcal{W}_1$. The rest of $(n-1)$ elements in $\mathcal{W}_1$ are chosen so that they are significantly smaller than p^n. We will take them to be all equal (so that they keep α as big as possible) and to be $p^n v^{n-k}$ with some k that will be discussed later on. Also, we will choose the elements in $\mathcal{W}_2$ to be $p^n v^{n-m}$ with some m that is small and independent of n. At this point we do not know which exact choice of k and m will maximize $\mathcal{E}^{\Pi}$, but fortunately the existing information about them is enough to deduce the asymptotic behavior we need.

With above described Π we have

$$\lambda = \frac{1 + (n-1)v^{2(n-k)}}{\left(1 + (n-1)v^{n-k}\right)^2}. \tag{A.21}$$

So, to have $\lambda \to 1$, nv^{n-k} must $\to 0$. With this condition and some algebraic manipulations employing Taylor expansions, we arrive at the following asymptotic expansion:

$$\frac{\mathcal{E}^{\Pi}}{p^n} = 1 - n^2 v^{n-k-m/2} C_n + \mathcal{O}\left[n^3 v^{2(n-k)} \right], \tag{A.22}$$

where $C_n = (1 - 1/n)^2 \left(v^{m/2} + v^k n/(n-1) \right)$ and is always $\mathcal{O}[1]$ since $v < 1$ and k and m are positive. With this, we rewrite (A.22) as

$$\frac{\mathcal{E}^{\Pi}}{p^n} = 1 - n^2 v^{n-k-m/2} C_n \left(1 + \mathcal{O}\left[n v^{n-k} \right] \right). \tag{A.23}$$

Having in mind that $nv^{n-k} \to 0$ and explicitly indicating the dependence of k and T (and hence v) on n we obtain from (A.23) the asymptotic condition of the positivity of $\mathcal{E}^{\Pi}$ in the following form:

$$1 \geq n^2 v_n^{n-k_n-m/2} C_n = e^{\ln C_n + 2\ln n - \frac{n-k_n-m/2}{T_{GME}/E}}. \tag{A.24}$$

From formula (A.24) it is now obvious that to maximize T_{GME}, k_n has to be as small as possible. So, whatever the k_n and m delivering the maximum are, they are finite numbers independent of n. Therefore,

$$T_{GME}^{\max} = \frac{nE}{2\ln n} + \mathcal{O}\left[\frac{nE}{(\ln n)^2}\right]. \tag{A.25}$$

Finally the energy input required for such a scaling can simply be calculated from the prior permutations Π alone, as all subsequent rotations are performed in a degenerate subspace. Adding the cost of all the permutations above gives the rather cumbersome formula for the energy cost of the W-state protocol as

$$\begin{aligned} W = E(1-e^{-\beta E})^{-n}\big((n-1)(e^{-\beta E} - e^{-\beta E(n-1)}) + (1-e^{-\beta E}) + ne^{-\beta E(n-3)} - \\ ne^{-\beta En} + (n^2-n)(e^{-2\beta E} - e^{-(n-2)\beta E}) + 3(e^{-\beta En} - e^{-\beta E(n-3)})\big) \end{aligned} \tag{A.26}$$

which while seemingly complicated due to the numerous required permutations still remains exponentially small in n for any $T > 0$.

The W-state is but an element of a larger set of Dicke states. Correspondingly, our W-state protocol can be straightforwardly generalized to Dicke state protocols. First, let us introduce the m excitation Dicke states for n qubits:

$$|D_m\rangle = \frac{1}{\sqrt{C_n^m}} \sum_{\{\alpha\}} |\{\alpha\}\rangle, \tag{A.27}$$

where $\{\alpha\}$s are the subsets of $\{i\}_{i=1}^n$ consisting of m elements, $|\{\alpha\}\rangle = \bigotimes_{i\in\{\alpha\}} |1\rangle_i \bigotimes_{j\in\{j\notin\{\alpha\}\}} |0\rangle_j$, and the summation runs over all C_n^m possible $\{\alpha\}$s. Accordingly, the Dicke state protocol is the one when one is allowed to create non-diagonal elements only in $\mathcal{D}_m$ – the subspace spanned by $|\{\alpha\}\rangle$s. In that case, the GME witness is as follows (**?**):

$$\begin{aligned} \mathcal{E}_m[\Omega] = \sum_{\{\gamma\}} \Big(|\langle\{\alpha\}|\Omega|\{\beta\}\rangle| - \sqrt{\langle\{\alpha\}| \otimes \langle\{\beta\}|\Pi_{\{\alpha\}}\Omega \otimes \Omega\Pi_{\{\alpha\}}|\{\alpha\}\rangle \otimes |\{\beta\}\rangle} \Big) - \\ n(n-m-1)\sum_{\{\alpha\}} \langle\{\alpha\}|\Omega|\{\alpha\}\rangle, \end{aligned} \tag{A.28}$$

where the set $\{\gamma\}$ is the collection of all possible $(\{\alpha\},\{\beta\})$ with $\{\beta\}\in\mathcal{D}_m$ and such that the intersection $\{\alpha\}\cap\{\beta\}$ contains $m-1$ elements. As is straightforward to check, $\{\gamma\}$ has $m(n-m)C_n^m$ elements. $\Pi_{\{\alpha\}}$ is a permutation operator which, acted on some $|0...1...0...1\rangle\otimes|1...0...0...1\rangle$, swaps the parts of the vectors corresponding to $\{\alpha\}$ so that it takes first vector to $\mathcal{D}_{m-1}$ and the second one to $\mathcal{D}_{m+1}$; e.g., $\Pi_{\{2,3\}}|01100\rangle\otimes|11000\rangle=|01000\rangle\otimes|11100\rangle$ (see (**?**) for more detailed explanations).

As above, the idea is to maximize $\mathcal{E}_m[U\Pi\Omega\Pi U^\dagger]$ over all unitaries U acting in $\mathcal{D}_m$ and permutations Π. Again, for a fixed Π one has to maximize $\sum_{\{\gamma\}}|\langle\{\alpha\}|\Omega|\{\beta\}\rangle|$, but since $\{\gamma\}$ does not run over all non-diagonal elements the form (A.19) may not necessarily be the optimal one. Nevertheless, since finding maximum of the sum of absolute values of the part of non-diagonal elements of a matrix appears to be a formidable task, we will use the form (A.19) as an ansatz. In what follows we will show that the asymptotic behavior for $T_{GME}^{\max}$ following from this ansatz is very close to the optimal one. As in the previous case, the permutation delivering the optimal asymptotics will be the one that puts p^n and p^nv^{n-k} (with $k\geq m$ finite but sufficiently big) in $\mathcal{D}_m$ and fills $\mathcal{D}_{m-1}$ and $\mathcal{D}_{m+1}$ with some p^nv^{n-l} (with sufficiently big and finite l). With this, after simple manipulations we arrive at

$$\mathcal{E}_m^\Pi=p^nm(1+(C_n^m-1)v^{n-k}-C_n^m(n-m)v^{n-k}-C_n^m(n-m)v^{n-l}+\mathcal{O}\left(n^{2m}v^{2n}\right)).\tag{A.29}$$

So the condition for the presence of genuinely multipartite entanglement, $\mathcal{E}_m^\Pi\geq 0$ reduces to (**?**)

$$e^{(m+1)\ln n-\frac{nE}{T}}\leq 1\tag{A.30}$$

whence we obtain

$$T\sim\frac{nE}{(m+1)\ln n}\tag{A.31}$$

implying that

$$T_{GME}^{\max}\geq\frac{nE}{(m+1)\ln n}\tag{A.32}$$

for large ns.

Now, returning to the question of how close to the optimal this scaling is, let us observe that the maximum for $\sum_{\{\gamma\}}|\langle\{\alpha\}|\Omega|\{\beta\}\rangle|$ is given by $\sqrt{(\lambda-1/N)N(N-1)}$ with N in this case being C_n^m (see (A.19) and the reasoning preceding it). This value for $\sum_{\{\gamma\}} |\langle\{\alpha\}|\Omega|\{\beta\}\rangle|$ is not necessarily unitarily achievable from the initial diagonal state but is clearly an upper bound for it. Proceeding as above with this ansatz we obtain

$$T_{GME}^{\max} \leq \frac{nE}{m \ln n} \tag{A.33}$$

showing that the initial ansatz (A.19) is quite reasonable and that in any case $T_{GME}^{\max} = \mathcal{O}\left(\frac{n}{\ln n}\right)$ for all m.

A.5. Fermionic systems: Correlation matrices, time evolution, and entropy

We consider Hamiltonians of the type

$$H = \sum_{i,j} c_{i,j} a_i^\dagger a_j \tag{A.34}$$

where the operators $a_i, a_i^\dagger$ satisfy the fermionic anti-commutation relations,

$$\{a_i, a_i^\dagger\} = \delta_{i,j}, \tag{A.35}$$

$$\{a_i, a_j\} = \{a_i^\dagger, a_j^\dagger\} = 0. \tag{A.36}$$

Since the matrix c in (A.34) is hermitian, it can be diagonalised by a unitary operator, $c = ADA^\dagger$, where $AA^\dagger = 1$ and $D = \mathrm{diag}\{E_1, ..., E_n\}$. The Hamiltonian then can be expressed as,

$$H = \sum_k E_k \eta_k^\dagger \eta_k, \tag{A.37}$$

with

$$\eta_k = \sum_j A_{j,k}^* a_j, \tag{A.38}$$

$$\eta_k^\dagger = \sum_j A_{j,k} a_j^\dagger. \tag{A.39}$$

The unitarity of A ensures that the transformation preserves the commutation relations,

$$\{\eta_k, \eta_l^\dagger\} = \sum_{i,j} A_{k,i} A_{l,j}^* \{a_i, a_j^\dagger\} = \delta_{k,l}. \tag{A.40}$$

where we used (A.36).

We will describe states within the framework of correlation matrices. Define the entries of the correlation matrix $\gamma(\rho)$ corresponding to ρ as

$$\gamma_a\left(\rho\right)_{i,j} = \mathrm{Tr}(a_i^\dagger a_j \rho). \tag{A.41}$$

Notice that the diagonal elements represent the occupation probabilities, or populations, of each fermion. The correlation matrix in the diagonal basis $\gamma_\eta(\rho)_{i,j} = \mathrm{Tr}(\eta_i^\dagger \eta_j \rho)$ is related to γ_a through $\gamma_\eta = A^T \gamma_a A^*$. The diagonal elements of γ_η, corresponding to the populations of the free fermions, play an important role, and we denote them by p_k,

$$p_k = \mathrm{Tr}(\eta_k^\dagger \eta_k \rho). \tag{A.42}$$

The time evolution of $\gamma(\rho)$ under H, $\rho(t) = e^{-\mathrm{i}Ht}\rho e^{\mathrm{i}Ht}$, can be easily computed in the Heisenberg picture,

$$\begin{aligned} \frac{\eta_k}{dt} &= \mathrm{i}[H, \eta_k] = -\mathrm{i}E_k \eta_k, \\ \eta_k(t) &= e^{-\mathrm{i}E_k t}\eta_k, \end{aligned} \tag{A.43}$$

where we have used $\{\eta_i, \eta_j^\dagger\} = \delta_{i,j}$ and $\eta_k^2 = 0$. Therefore, on the one hand, it follows that

$$\gamma_\eta(\rho(t)) = e^{\mathrm{i}tD}\gamma_\eta(\rho)e^{-\mathrm{i}tD} \tag{A.44}$$

with $D = \mathrm{diag}\{E_1, ..., E_n\}$. In the original basis it reads,

$$\gamma_a(\rho(t)) = U\gamma_a(\rho)U^\dagger \tag{A.45}$$

with $U = A^* e^{\mathrm{i}tD} A^T$. On the other, the time averaged state, which is defined as,

$$\langle\rho\rangle_t = \lim_{T\to\infty} \frac{1}{T}\int_0^T \rho(t), \tag{A.46}$$

is given simply by

$$\gamma_\eta(\langle\rho\rangle_t) = \langle\gamma_\eta(\rho)\rangle_t = \Gamma\left[\gamma_\eta(\rho(t))\right] \tag{A.47}$$

where Γ corresponds to a de-phasing operation. In fact, this state corresponds to the GGE where the conserved quantities are the energy modes $\eta_k^\dagger \eta_k$, i.e.,

$$\omega_{\mathrm{GGE}}(\rho, H^{(i+1)}, \{\eta_k^{(i+1)\dagger}\eta_k^{(i+1)}\}) = \langle\rho\rangle_t\,. \tag{A.48}$$

The entropy of ρ can be calculated as

$$S(\rho) = \sum_k H(d_k^{(i)}). \tag{A.49}$$

where d_k are the eigenvalues of $\gamma(\rho)$, and $H(p) = -p\ln p - (1-p)\ln(1-p)$.

A.6. Work extraction for free fermions and unrestricted Hamiltonians

Here we find a bound for work extraction protocols, which, as discussed in the main text, is equivalent to finding a lower bound on the final energy, $\mathrm{Tr}\,(\omega^{(N)}_{GGE}H^{(0)})$, with $H=\sum_k \epsilon^{(0)}_k \eta^\dagger_k \eta^{(0)}_k$. From our considerations in Section A.5, it follows that under the joint operation of a quench,

$$H^{(i)}=\sum_{i,j} c^{(i)}_{i,j} a^\dagger_i a_j \mapsto H^{(i+1)}=\sum_{i,j} c^{(i+1)}_{i,j} a^\dagger_i a_j, \tag{A.50}$$

followed by an equilibration process, our effective description in terms of GGE states takes the form

$$\gamma_a(\omega^{(i+1)}_{GGE})=A^*_{(i+1)}\Gamma\left[A^T_{(i+1)}\gamma_a(\omega^{(i)}_{GGE})A^*_{(i+1)}\right]A^T_{(i+1)} \tag{A.51}$$

where Γ is a de-phasing operation, and $c^{(i+1)}=A_{i+1}DA^\dagger_{i+1}$, with D is a diagonal matrix. Let $\{d^{(i+1)}_k\}$ and $\{d^{(i)}_k\}$ bet the eigenvalues of $\gamma_a(\omega^{(i+1)}_{GGE})$ and $\gamma_a(\omega^{(i)}_{GGE})$, respectively. Under (A.51), they are related through a doubly stochastic matrix,

$$d^{(i+1)}_k=\sum C_{k,l}d^{(i)}_l \tag{A.52}$$

with $\sum_k C_{k,l}=\sum_l C_{k,l}=1$. Therefore, the eigenvalues of the final state $\gamma_a(\omega^{(N)}_{GGE})$ can also be expressed as a stochastic combination of the eigenvalues of $\gamma_a(\rho^{(0)})$, $\{d^{(0)}_k\}$. It now follows from basic notions of the theory of majorization that,

$$\mathrm{Tr}\,(\omega^{(N)}_{GGE}H^{(0)})\geq\sum_{k=1}^{n}(d^{(0)}_k)^{\downarrow}(\epsilon^{(0)}_k)^{\uparrow}=\mathrm{Tr}\,(\omega^*_{GGE}H^{(0)}) \tag{A.53}$$

where $^\uparrow$ and $^\downarrow$ reflect lists ordered in increasing (decreasing) order. This provides the bound (8.60).

We now construct an explicit protocol that achieves this bound in the limit $N\to\infty$, where N is the number of quenches performed. Let $\gamma_a(\rho^{(0)})$ be the correlation matrix of $\rho^{(0)}$ as in (A.41). First, find some U that diagonalises $\gamma(\rho^{(0)})$,

$$U\gamma(\rho^{(0)})U^\dagger=D, \tag{A.54}$$

and make a quench to

$$H^{(1)}=U^T H^{(0)} U^*. \tag{A.55}$$

Since $\gamma(\rho^{(0)})$ is diagonal in the new basis, it follows that $\omega_{\mathrm{GGE}}^{(1)} = \rho^{(0)}$, i.e., the state is not changed during the equilibration process. Now, slowly rotate back to the original Hamiltonian, by performing $N/2$ quenches (followed by equilibration processes) until $H^{(0)}$ is reached. At the end the state, $\rho^{(N/2)}$ is (approximately) diagonal with respect to the original Hamiltonian, $H^{(0)}$. Next, find some V that order the populations of $\gamma(\rho^{(N/2)})$, so that $V\gamma(\rho^{(N/2)})V^\dagger$ satisfies (8.60). As before, perform a quench to $H^{(1)} = V^T H^{(0)} V^*$, and slowly come back to the original Hamiltonian by performing $N/2$ quenches. This process will render the desired final state ω_{GGE}^* in the limit of infinitesimally slow transformations, i.e., in the limit $N \to \infty$. The optimal protocol is therefore reversible, and it agrees with our intuition that slow processes are better for work extraction.

Importantly, note that these results for the free fermions are completely analogue to the case of time average equilibrium state, as detailed in Sec. 8.6. Indeed, the optimal protocol of work extraction resembles the one discussed in Sec. 8.6. However, it should be stressed that the GGE equilibration model considered for free fermions does not coincide in general with the time averaged state. Indeed, this difference can be highlighted by looking at the final state obtained for the time average model in comparison with the final state of the GGE equilibration for free fermions. In the former, one ends up with a passive state. This implies, for n fermions, 2^n energy populations decreases with the energy. On the other hand, for the GGE model of equilibration considered here, the final state ω_{GGE}^* is such only the n populations of the free fermions need to be in decreasing order.

For example, consider a three-fermion system with Hamiltonian

$$H = \epsilon_1 \eta_1^\dagger \eta_1 + \epsilon_2 \eta_2^\dagger \eta_2 + \epsilon_3 \eta_3^\dagger \eta_3 \tag{A.56}$$

and a state ρ with $\mathrm{Tr}(\eta_i^\dagger \eta_i \rho) = p_i$ with $i = 1, 2, 3$. The quantum state ρ and H can be written as

$$\begin{aligned} H =& \mathrm{diag}\{0, \epsilon_1, \epsilon_2, \epsilon_3, \epsilon_1+\epsilon_2, \epsilon_2+\epsilon_3, \epsilon_1+\epsilon_3, \epsilon_1+\epsilon_2+\epsilon_3\} \\ \rho =& \mathrm{diag}\{(1-p_1)(1-p_2)(1-p_3), p_1(1-p_2)(1-p_3), \\ & p_2(1-p_1)(1-p_3), p_3(1-p_1)(1-p_2), p_2 p_1(1-p_3), \\ & p_2 p_3(1-p_1), p_1 p_3(1-p_2), p_1 p_2 p_3\}. \end{aligned} \tag{A.57}$$

If we now choose $\epsilon_1 = 1$, $\epsilon_2 = 2$, $\epsilon_3 = 2.5$; and $p_1 = 0.4$, $p_2 = 0.3$, and $p_3 = 0.1$; we obtain that ρ is not passive but has the form of ω_{GGE}^*. The origin of the difference is the set of operations in which every state is defined. Passive states arise as optimal states for work extraction protocols if any unitary operation can be performed to the system, or, equivalently, every cyclic process in which the system remains thermally isolated. On the other hand, states ω^*_{GGE} become optimal when the set of operations corresponds to (arbitrary) quenches to quadratic Hamiltonians, which is in general more constraint that the set of unitary operations. Within this constrained set of operations, they become optimal.

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