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A THEORY OF THERMODYNAMICS FOR NANOSCALE QUANTUM SYSTEMS

Proefschrift

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A law is more impressive the greater the simplicity of its premises,
the more different are the kinds of things it relates,
and the more extended its range of applicability.
Therefore the deep impression that classical thermodynamics made upon me.
It is the only physical theory of universal content, which I am convinced,
that within the framework of applicability of its basic concepts will never be overthrown.

Albert Einstein

That is what the Scriptures mean when they say,
"No eye has seen, no ear has heard, and no mind has imagined
what God has prepared for those who love him."

1 Corinthians 2:9

SUMMARY

Thermodynamics is one of the main pillars of theoretical physics, and it has a special appeal of having wide applicability to a large variety of different physical systems. However, many assumptions in thermodynamics apply only to systems which are bulk material, i.e. consisting a large number of microscopic classical particles. Due to the advancement of designing nanoscale engines, especially in the light of devices that are used today in the processing of quantum information, is thermodynamics still applicable? Can we refine the core principles of thermodynamics to suit such nanoscale quantum systems as well?

The central aim of this thesis is to construct a theory of thermodynamics that holds for nanoscale quantum systems, even those as small and simple as a single qubit. We do this by starting out from the core basics of quantum theory: unitary dynamics on closed quantum systems. We adapt a resource theoretic approach inspired by quantum information theory, which defines the quantum states and operations allowed to be used in a thermodynamic evolution. With this framework that naturally adopts the first law as an energy preserving condition, we show the refinement of both the zeroeth and second law of thermodynamics. The zeroeth law explains the physical significance of the Gibbs thermal state. On the other hand, we show that the second law sees refinement in the quantum nanoregime: instead of having the free energy as the sole quantity dictating the possibility of a thermodynamic state transition, we derive a family of generalized free energies that also constitute necessary conditions for a transition to occur. Moreover, these conditions become sufficient for states which are block-diagonal in the energy eigenbasis.

In this thesis, we also brought our approach of thermodynamics to the next step: we apply our findings on the second laws, in order to analyze the maximum achievable efficiency for quantum heat engines. In classical thermodynamics, the Carnot efficiency has been long known as the theoretical maximum which does not depend on the specific structure of the thermal baths used, but only on its temperature. With the additional free energies we discover, we show that although quantum heat engines may achieve the Carnot efficiency, such an achievability is no longer independent of the Hamiltonians of the thermal baths. In other words, we find additional restrictions that surface in the study of quantum nanoscale heat engines, which are a direct consequence of the generalized second laws. This has provided us with a deeper understanding into the fundamental limitations of how efficient devices can be made in the realm of microscopic quantum systems.

SAMENVATTING

Thermodynamica is één van de grootste pijlers van de theoretische natuurkunde, en heeft de aantrekkelijke eigenschap wijd toepasbaar te zijn op een grote verscheidenheid aan systemen. Maar vele aannamen in de thermodynamica zijn alleen van toepassing op systemen van bulk materiaal d.w.z. bestaande uit een groot aantal microscopische, klassieke deeltjes. Door de vooruitgang in het ontwerpen van machines on de nanoschaal, en in het speciaal de machines die vandaag de dag worden gebruikt in de kwantum informatica, is de vraag is de thermodynamica nog toepasbaar? Kunnen we de centrale principes van de thermodynamica zo verfijnen dat ze ook toepasbaar zijn op de nanoschaal?

Het hoofddoel van deze thesis is om een thermodynamica theorie op te stellen die toepasbaar is voor alle kwantum systemen op de nanoschaal, zelfs zulke kleine systemen als een enkele qubit. Om dit te bereiken starten we met de basis van de kwantum informatica: unitaire dynamiek op afgezonderde kwantum systemen. We gebruiken een aangepaste vorm van ?resource theoretic approach? geïnspireerd door kwantum informatie theorie, wat de kwantum staten en operaties definieert die zijn toegestaan tijdens een thermodynamische evolutie van een systeem. In dit framewerk wordt de eerste wet als de natuurlijke energie preserverende conditie wordt aangenomen laten we de verfijning van de nulde en tweede wet van de thermodynamica zien. De nulde wet laat de natuurkundige significantie van de Gibbs thermale staat. Aan de andere kant laten we ook zien dat de tweede wet verfijnd wordt in het kwantum nano regime: in plaats van alleen de vrije energie als enige variabele die de mogelijkheid van een thermodynamische staat transitie bepaalt, lijden we een hele familie van gegeneraliseerde vrije energieën af die ook noodzakelijke condities geven voor het plaatsvinden van een transitie. En deze condities zijn voldoende voor staten die blokdiagonaal zijn in de energie eigenbasis. In deze thesis brengen we ook onze verfijning van de thermodynamica tot het volgende niveau: we passen onze bevindingen over de tweede wet toe, om de maximaal behaalbare efficiency van een kwantum hitte motor te analyseren.

In de klassieke thermodynamica, is de Carnot efficiency voor lange tijd al bekend als het theoretisch maximum, ongeacht de specifieke structuur van de hitte bronnen maar alleen afhankelijk van hun temperatuur. Met de extra vrije energieën die wij hebben ontdekt, laten we zien dat, alhoewel sommige kwantum hitte motoren nog steeds de Carnot efficiency kunnen halen, dit vermogen niet langer onafhankelijk is van de Hamiltoniaan van de hitte bron. In andere worden, we vinden extra restricties die verschijnen bij het bestuderen van kwantum nanoschaal hitte motoren en die een direct gevolg zijn van de gegeneraliseerde tweede wet. Dit geeft ons een beter begrip van de fundamentele limieten op hoe efficiënt machines kunnen worden op de schaal van microscopische kwantum systemen.

List of Publications

Chapter 4 of this thesis is based on the following publication:

The second laws of quantum thermodynamics
Fernando G.S.L. Brandao, Michal Horodecki, Nelly Huei Ying Ng, Jonathan Oppenheim, Stephanie Wehner
Proceedings of the National Academy of Sciences 112, 3275
February 2015

Chapter 5 is based on the following publication:

Limits to catalysis in quantum thermodynamics
Nelly Huei Ying Ng, Laura Mančinska, Cristina Cirstoiu, Jens Eisert and Stephanie Wehner
New Journal of Physics, Volume 17
(Focus Edition on Quantum Thermodynamics)
August 2015

Chapters 6 and 7 are based on the following preprints:

The maximum efficiency of nano heat engines depends on more than temperature
Mischa Woods, Nelly Huei Ying Ng, Stephanie Wehner
arXiv:1506.02322
Submitted to Physical Review X for peer review

Surpassing the Carnot efficiency with extraction of imperfect work
Nelly Huei Ying Ng, Mischa Woods, Stephanie Wehner
arXiv:1606.05532
submitted to New Journal of Physics for peer review

During her graduate studies, the student also completed the following publications:

Maximization of Extractable Randomness in a Quantum Random-Number Generator
Jing Yan Haw, Syed M. Assad, Andrew M. Lance, Nelly Huei Ying Ng, Vikram Sharma, Ping Koy Lam, Thomas Symul
Physical Review Applied 3 (5), 054004 May 2015

An experimental implementation of oblivious transfer in the noisy storage model
Chris Erven, Nelly Huei Ying Ng, Nikolay Gigov, Raymond Laflamme, Stephanie Wehner,

Gregor Weihs
Nature Communications 5, 3418 March 2014

Experimental implementation of bit commitment in the noisy-storage model
Nelly Huei Ying Ng, Siddarth K Joshi, Chia Chen Ming, Christian Kurtsiefer, Stephanie Wehner
Nature Communications 3, 1326 December 2012

Min-entropy uncertainty relation for finite-size cryptography
Nelly Huei Ying Ng, Mario Berta, Stephanie Wehner
Physical Review A 86 (4), 042315
October 2012

CONTENTS

1

INTRODUCTION

We give an overview of thermodynamics, starting from its earliest phenomenological form involving only macroscopic observables of classical bulk systems, to how it has been extended to include devices in the microscopic regime. Even with all the remarkable recent progress, a complete theory of thermodynamics that holds also for small quantum systems is still much warranted. This provides the main motivation of the research presented in this thesis. We explain how concepts from information theory, both classical and quantum, have contributed to foundational understanding of thermodynamical interactions. This motivates the use of approaches and concepts in quantum information theory, in order to build a theory of thermodynamics that holds for nanoscale systems which obey the laws of quantum mechanics. Lastly, an outline of the thesis is presented.

1

1.1. CLASSICAL THERMODYNAMICS: A FUNDAMENTAL PILLAR OF THEORETICAL PHYSICS

"The second law of thermodynamics is, without a doubt, one of the most perfect laws in physics. "
E.H.Lieb and J.Yngvason, [1]

If research in physics is likened to a hiking trail aimed at reaching undiscovered heights, then at first glance, the field of thermodynamics is an odd place to begin the journey. Classical thermodynamics, being one of the main pinnacles of theoretical physics, was established, further developed and applied for almost two centuries. Even to this day, it is still adored by many modern-day physicists as being "perfect" and "universally applicable". Even Albert Einstein himself expressed an utmost confidence in it, amongst all the other physical theories (see epigraph). However, the hiker must bear in mind that the higher the pinnacle, the larger the whole mountain. Unexplored territory remains, where the scenery of the pinnacle changes, making the journey all the more interesting.

Furthermore, it is worth recalling that the historical motivation for this branch of study was a down-to-earth one, aiming to improve the performance of then existing engines. Therefore, thermodynamics from the beginning was *phenomenological*, concerning itself with *macroscopic observables* of large systems, such as the volume, pressure, energy and their relation with each other in the *steady-state limit*. With the advancement of technology, the workings of machines/devices have moved far beyond such a regime. It is thus inevitable, that we re-examine the roots of thermodynamics in the light of these changes.

PHENOMENOLOGICAL THERMODYNAMICS

We begin our journey by first recalling what we know so far about the fundamental principles of equilibrium thermodynamics. A variety of formulations for these laws can be found in any standard classical thermodynamic textbook [2–5].

Box 1.1.1: The laws of classical thermodynamics

Zeroeth law (Transitivity of thermal equilibrium):
Two systems are considered to be in thermal equilibrium if there is no net heat flow between them, even when they are connected to each other so that heat may flow freely. If system A is in thermal equilibrium with B, and system C is also in thermal equilibrium with B, then A is in thermal equilibrium with C.

First law (Energy conservation):
In any process where energy flows in and out of a system, its internal energy changes according to the law of energy conservation.

Second law (Asymmetry in time):
The disorderliness of an isolated system always increases in time.

Third law (Absolute zero temperature):
A system can never reach the absolute zero temperature within a finite number of steps/processes and finite amount of time.

These laws constitute the core of the thermodynamic framework, and within these laws, the second law in particular has a unique role, being one of the very first principles observed and applied in the discussion of heat engines. Not only was the second law originally stated as an empirical observation of nature, it has been formulated in many different ways by the founding fathers of thermodynamics/statistical physics. The earliest statements come from Lord Kelvin and Rudolph Clausius, which can be shown to be equivalent to each other [2].

- **Kelvin statement [6] (1851)**
  "It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects."

- **Clausius statement [7] (1854)**
  "Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time."

At the heart of the second law is the distinction of energy into two parts: "work" as ordered/useful energy (the "mechanical effect" in Kelvin's statement), versus "heat" which is disordered/wasted energy. The statements made by Kelvin and Clausius have arisen from keen observations on systems encountered in everyday life: bulk materials (usually fluids such as water, steam or other gasses) comprising of many interacting classical particles. Earlier in 1824, Sadi Carnot, who was often regarded as the "father of thermodynamics", developed the concept of reversibility and Carnot cycles for heat engines, in order to understand the maximum possible efficiency/power output of heat engines. The works of Kelvin and Planck of the second law have allowed for the derivation of the maximum efficiency any heat engine could possibly achieve, now known as the Carnot efficiency.

Another one of the fundamental observations in thermodynamics, is the fact that most bulk systems have the tendency to evolve towards a steady state where the macroscopic variables do not change. Such a state is denoted as the *thermodynamic equilibrium state*, and is characterized by a real-valued parameter called the temperature T (in this thesis, we more often deal with the inverse temperature, $\beta = \frac{1}{k_B T}$, where k_B is a constant parameter known as the Boltzmann constant). Two systems at their respective thermal equilibrium can be compared with each other by this temperature; and if they have the same temperature, there will be no net heat exchange between the systems. Such a parametrization, where its transitivity is stated as the zeroeth law, is used to define "coldness" and "warmness" of systems (such as in the Clausius statement).

Today, the second law is widely used in areas such as chemistry, condensed matter, and almost all braches of engineering/physics. Even outside of physics, the second law can be used to provide insights into the dynamical processes of evolution theory or even economics [8, 9], hinting at an underlying, more foundational mathematical structure in which the second law is a consequence of. Due to the successful record of phenomenological thermodynamics in describing the physical world, since its emergence there has been a large amount of effort to ground its observations in a rock solid foundation of mathematical structure and physical principles that describe the behaviour of microscopic particles.

1

STATISTICAL MECHANICS AND AXIOMATIC THERMODYNAMICS

In the later 20th century, a microscopic description of thermodynamical processes was formulated in the field of statistical physics. These studies were pioneered by physicists such as James Clerk Maxwell and Ludwig Boltzmann. The central thesis of statistical mechanics is that *macroscopic behaviour* of fluids and gases observed in thermodynamics, is a result of basic principles of kinematics, with a main additional assumption on the ensemble of *microscopic particles*. This assumption is called the principle of equal a priori probabilities (PEAPP), namely that for a system at equilibrium, all accessible microstates of the system are equally likely.

From this perspective, the second law can be formulated in terms of the *entropy* of a system P,

$$H(P) = \sum_i p_i \ln \frac{1}{p_i}, \tag{1.1.1}$$

where the summation runs across all possible microstates of the system. This quantity measures the amount of "disorder" in the system, as we have encountered in Box 1.1.1. The second law of thermodynamics is then re-formulated as follows: for any isolated system P (also known as the microcanonical ensemble), the entropy of the system can only increase in time. A system at equilibrium is therefore the state with the maximum amount of entropy. This principle, when applied to studying a system that exchanges energy when interacting with an environment of inverse temperature β, leads to another familiar formulation of the second law:

- Consider a system P in heat contact with a thermal bath at fixed inverse temperature β. The free energy of such a system,

$$F(\rho) = \langle E \rangle_P - \frac{1}{\beta} H(P), \tag{1.1.2}$$

  can only ever decrease in time, where $\langle E \rangle_P$ is the average energy of the system. This free energy quantity also gives the amount of work that can be extracted from the system.

It is certain that one always finds physical assumptions on the systems that lie outside of classical mechanics, such as ergodicity, adiabaticity, short-range interactions etc, in order to derive the entropy function and the second law. These assumptions hold, at least approximately for most classical bulk systems. Even for the most exotic types of material (real gases, non-Newtonian fluids etc), at the very least the number of particles involved are truly huge, i.e. of the order of Avogadro's constant ($\approx 6 \times 10^{23}$), where statistics becomes an extremely powerful tool in singling out the average behaviour of the system as a whole. On the other hand, there have been axiomatic approaches towards thermodynamics, which attempt to separate out the physical arguments from the derivation of the second law, by instead presenting a set of mathematical axioms for the derivation of entropy function [1, 10].

STOCHASTIC THERMODYNAMICS

Leaving the realm of equilibrium thermodynamics, one immediately realizes that obviously equilibration is not a generic description of systems at all times. Systems are easily pushed out of equilibrium by operations from an observer, for example performing compression on

a mole of gas, or simply mixing two systems which were at different temperatures. To deal with small deviations from equilibrium, linear response theory is a commonly used aproach in approximately quantifying non-equilibrium behaviour.

The first quest to refining thermodynamics happened when attempting to move from linear response theory to genuinely non-equilibrium dynamics [11]. The motivation for developing such a theory, is due to the fact that classical engines have became intricate enough, such that they are affected non-trivially by energy fluctuations. Such fluctuations form a time-dependent driving potential for the system, where the potential changes over an amount of time which is of the same magnitude with the equilibrium time scale of the system. This implies that the system of interest is constantly pushed out of equilibrium. Also, often in such cases, the system of interest might only consist of a handful of particles, and the resolution of our analysis may go all the way down to the trajectories of an individual particle through its phase space, such as the motion of a single Brownian particle driven by random forces (collision with smaller molecules) from its surroundings. Examples of such classical engines today are Brownian ratchets, biopolymers, molecular motors etc [12, 13].

Dyanmical models have largely been developed to describe non-equilibrium processes. In particular, the evolution of systems which obey Markovian dynamics can usually be described as differential equations such as Master equations. Our understanding of the second law, upon scrutiny, has also seen refinement: fluctuation theorems say that for a large class of models for classical systems, when analyzing the trajectories of the system through its phase space, the second law (i.e. the increase of entropy w.r.t. time) is a statistical law that is obeyed with high probability. Well known examples of fluctuation theorems include the Jarzynski relation [14], and Crooks theorem [15]. These relations have been proven for a large class of classical systems (in particular, all Markovian systems [16], and certain non-Markovian systems with additional assumptions [17]).

These investigations have shown us that traditional thermodynamics has been radically transformed for devices that operate in the nanoscale regime. However, the quest is unfinished, and a larger revolution of thermodynamics is still on its way.

THE CHALLENGE AHEAD: REVAMPING THERMODYNAMICS FOR NANOSCALE QUANTUM SYSTEMS

The first quantum revolution happened in the early 20th century, shocking physicists with new rules that govern elementary particles. However, after recovering from that initial shock, a new wave is rising: by engineering and controlling quantum systems, quantum physics is changing the way we handle information. Novel advantages are being harnessed in the context of computational speed and communication security. These advantages have no precedence in the classical world. Quantum information, both theory and experimental, therefore brings us to the second quantum revolution [18], where physicists are making use of quantum mechanics to discover new ways of processing information.

In these endeavours, we deal with a large variety of microscopic quantum systems, such as quantum dots, superconducting qubits, cold atoms and single-photons. Current efforts are aimed at preserving the quantum information encoded in these systems, while increasing the accuracy of manipulating the state at will. In the future, if we envision constructing a scaled-up quantum architecture, we will inevitably need to construct small quantum machines which can execute control over different parts of the system. An example of such

a machine is a theoretical proposal of quantum fridges [19–21], which aim to achieve regional cooling on parts of the quantum system, or a nanoscale heat engine, which has been recently realized experimentally in the setting of a single trapped ion [22]. However, it is not clear if the principles of classical thermodynamics can find their ground in the quantum nanoscale regime. These systems may consist of a mere handful of qubits. Fundamentally, they are governed by reversible quantum dynamics. Some of the specific dissipative models in stochastic thermodynamics might be extendable to the quantum regime, however most of these systems still do not conform to the assumptions traditionally made when deriving the second law. Even to the extreme, due to the fragility of quantum states (since they decohere rapidly while interacting with the environment), when handling quantum information we often desire single-shot descriptions of the performance of tasks using these systems. These collective challenges dim the usefulness of statistical methods.

Therefore, the question is: do the laws of thermodynamics emerge when dealing with such quantum systems? Does the second law, in particular, still hold?

1.2. INFORMATION THEORY AND THERMODYNAMICS

As outlined in [23], any theory that seamlessly connects the microscopic mechanical laws to descriptions of macroscopic phenomena should satisfy the following: 1) free of all mathematical objections, 2) involves no arbitrary, additional assumptions, and 3) provides explanations for both equilibrium thermodynamics and non-equilibrium, irreversible processes. Historically, 2) was almost impossible in classical statistical mechanics. However, information theory is precisely a field of study which investigates the limits of processing information *independent* from the physical systems that encode such information. Therefore, it has offered us new fundamental insights into building a fully general theory of thermodynamics. For example, the maximum entropy principle developed by Jaynes [23, 24] is one of the first contributions of information theory in thermodynamics. Jaynes showed that the emergence of the Gibbs state can be understood as a statistical inference that assumes full ignorance (therefore maximum entropy) about the state, under the constraints of known macroscopic variables or conserved quantities such as average total energy. Quoting [23], Jaynes concludes that "statistical mechanics need not be regarded as a physical theory dependent on its validity on the truth of additional assumptions not contained in the laws of mechanics (such as ergodicity, metric transitivity, equal a priori probabilities etc)".

Another issue that triggered the information theoretic approach to thermodynamics was the paradox of Maxwell's demon, which provided a way to seemingly violate the second law of thermodynamics using additional information [25]. In this paradox, a "demon" who has the ability to measure and obtain information about microscopic properties of individual particles (for example the velocity or position of gas molecules), may violate Clausius's statement by creating a temperature difference between two initially equilibrated systems (effective allowing heat flow from cold to hot bodies). Therefore, one observes from this paradox that since the demon is given access to more information about the system, it can make use of that information to violate the second law. Another similar, well known example is that of a Szilárd engine [26], which illustrates the possibility of extracting work (from a heat bath), given access to one bit of information. The answer to these paradigms have revealed a connection between information and energy: information processing tasks which

are irreversible[1] cannot be carried out without some inevitable consumption of work (and by conservation of energy, generation of heat). On the other hand, if one has access to an amount of information (encoded in a physical system), this information may be exhausted by allowing the system to interact with a bath, and work can be extracted. This is known as the Landauer's principle, originally studied for the case of information encoded in a particle trapped in a double-well potential [27], and subsequently derived in more generality [28–30]. Landauer's principle has far-reaching implications: in thermodynamics, it introduces a degree of subjectivity and the perspective of an observer which is potentially correlated with the system of interest. On the other hand, in computer science, it implies that for irreversible computation processes, heat dissipation is fundamentally inevitable, and therefore poses a practical problem of energy consumption in the design of computing devices.

QUANTUM INFORMATION THEORY

The community has seen a few important examples of advancements in quantum thermodynamics, which were contributed by concepts and tools in quantum information theory:

1. Addressing assumptions in classical statistical mechanics
   The *principle of equal a priori probabilities* (PEAPP), as we have seen, is one of the central assumptions of statistical mechanics. Such a principle, though being extremely useful in statistical physics, is inexplicable by itself, since it assumes a subjective ignorance about the state of the system. However, in the quantum information theoretic approach to statistical mechanics, there has been a deepening in the understanding of this principle, by linking the previously assumed subjective ignorance to the objective existence of entanglement. In short, it has been shown that for any typical, pure quantum state A of large dimension d_A, the reduced state of a small subsystem B is likely to be highly entangled with the rest of system A. Furthermore, entanglement is *monogamous*: if B is highly entangled with A, then to any other system C without access to A, system B by itself appears to be in a highly disordered state. This implies that system B (approximately) satisfies PEAPP. Furthermore, the smaller $d_B \ll d_A$ is, the closer system B is to the state that satisfies PEAPP. The reader may refer to the following review papers [31, 32] for a detailed survey on typical quantum states.

2. Conditions and time scales for equilibrium and thermalization of quantum systems
   When attempting to derive the principles of thermodynamics from quantum mechanics, an obvious problem is to why unitary, reversible evolutions in quantum theory give rise to the observation of irreversible dynamics for macroscopic systems. Under what conditions do quantum systems equilibrate? If equilibration occurs, what is the steady state, and what are the time scales for equilibration? These questions in quantum thermodynamics aim to rigorously explain the frequent emergence of Gibbs states as the equilibrated state. Tools in quantum information theory such as decoupling theorems [33] and Lieb-Robinson bounds [34, 35] have been applied in order to provide conditions on the Hamiltonian and initial state for thermalization, where time scales of thermalization depend on entropic measures of the state. In particular, relatively short time scales

[1] An example of such a process is erasure, which is the resetting of any memory state to a fixed, predetermined state. Erased information cannot be recovered, and therefore the process is irreversible.

for equilibration have also been proven for most randomly chosen Hamiltonians, initial states, and also by considering the expectation values of generic observables [33, 36–40].

3. Resource theories
How would a quantum system out of equilibrium evolve from one state to another while interacting with its thermal environment? The resource theory approach constitutes generic models that are aimed at resolving this problem. Such an approach starts by first defining a set of operation and states that can be performed/generated at no cost (commonly referred to as *free operations* and *free states*), in order to derive transition conditions between non-equilibrium states. With such state transition conditions, one can then compare different states with each other, by saying that a state ρ is more "valuable" than σ if $\rho \to \sigma$ can be achieved by the predefined free operations and states. This perspective has been extremely successful in several aspects of quantum information, such as the study of entanglement, purity or coherence as different "resources" [41–43]. These frameworks are discussed in depth later in Chapter 3 of this thesis, and we shall see that in thermodynamics, the main resource involved is work – ordered energy.

4. Thermodynamic protocols such as work extraction/cooling.
The study of quantum heat engines usually involves the explicit construction of a certain quantum system that, by interacting with multiple thermal baths, undergoes a cycle in which at the end, energy (in particular, work) is produced [44]. Building on Landauer's principle that having information allows for the extraction of work, protocols for work extraction and their optimality can be analyzed by using known results in data compression [45]. Qubit heat engines/refridgerators have also been proposed and analyzed [19], and it has been shown that the use of entanglement and quantum coherence may enhance the performance of those systems [20].

1.3. THESIS OUTLINE

Research Motivation and Summary

The central aim of the research presented in this thesis, is to start out only from the core principles of quantum theory, and derive laws that dictate the possibility of a thermodynamic state transition for arbitrary quantum states.

We describe the evolution of composite quantum systems via energy preserving unitary dynamics, further allowing for additional quantum ancillas to serve as machines/catalysts. We derive a set of conditions that tell us if a state transition $\rho \to \rho'$ may happen through a thermodynamical process. Subsequently, we apply these laws to study the maximum achievable efficiency for a quantum heat engine in the nanoscale regime.

In short, this thesis highlights the departure of quantum thermodynamics from the standard second law as we know it, and explicitly derives the consequences of such a departure, specifically on the maximum efficiency of heat engines.

In Chapter 1, an introduction to the problem of reconstructing thermodynamics for

quantum systems is given. In view of the contributions of information theory in thermodynamics, we see a newly rising approach to the task. With these motivations in mind, we give a brief overview of both classical and quantum information theory in Chapter 2. This chapter, however, is not aimed at providing an exhaustive overview of the achievements/essence in quantum information theory by itself. Instead, its aim is two-fold: 1) to introduce the concepts of information theory which will be useful in the application towards thermodynamics, and 2) to define all notations/conventions used throughout this thesis.

Chapter 3 introduces the framework of *thermal operations*, that starts out assuming only the very basic principles of quantum mechanics by using an information-theoretic approach, with the goal of describing how a quantum system interacts with its immediate, thermal surroundings. The problem of how to define work in the quantum nanoregime is also addressed, by giving a review of several ways to quantify work, especially focusing on models of storage systems for work.

Chapters 4-7 contain the main scientific contributions of this thesis. Chapter 4 considers the inclusion of ancillary *catalysts* in thermal operations, and derive state transition conditions which can be phrased in terms of generalized free energies. It is shown that these generalized free energies are monotonic under catalytic thermal operations, thus forming a set of necessary conditions for state transition. Moreover, these conditions are sufficient when considering states that are incoherent in the energy eigenbasis.

Chapter 5 turns to the case where catalysts are returned not exactly, but with some small error from its original state. We investigate different measures of such errors, and show that they lead to different subsets of the generalized second laws as state transition conditions. We define the notion of *thermal embezzling*, which is the trivialization of all state transition conditions by a small catalyst error, and proceed to investigate both the power and limitations of thermal embezzling, especially under certain physical constraints.

In Chapter 6, we construct a generic model of a quantum heat engine, and show how a heat engine cycle corresponds to the occurance of a state transition via catalytic thermal operations. This provides a way for the second law(s) to be applied in the derivation of heat engine efficiency. We provide a way of quantifying the quality of energy extracted, by categorizing different types of work according to the ratio $\frac{\Delta S}{W_{\text{ext}}}$, where ΔS is the induced change in entropy and W_{ext} is the amount of extracted energy. Such a characterization allowed us to define the following types of work: 1) perfect, 2) near perfect, and 3) imperfect work. We then apply the second law for macroscopic thermodynamics, and recover the results of Sadi Carnot, in the case of pearfect work and near perfect work extraction.

Chapter 7 then turns to apply the generalized second laws derived in Chapter 4 of this thesis, for the setting of our quantum heat engine. We find significant departures from Carnot's results when these generalized second laws for the quantum nanoregime are involved. We prove that Carnot efficiency remains as a theoretical maximum for all heat engines, and it may still be achieved under additional conditions, that depend on the Hamiltonian of the baths.

The thesis concludes in Chapter 8 with a summary of its contributions, with an outlook of open problems which are of potential future interest to the community.

2

PRELIMINARIES IN CLASSICAL AND QUANTUM INFORMATION

This chapter serves as a reference that contains the basic mathematical preliminaries and notation used throughout the thesis. From classical random variables to quantum density matrices, we see how information (both classical and quantum) may be quantified. We also see several entropic quantities and their properties.

In this chapter, we introduce the basic tools and notation used throughout this thesis. We start in Section 2.1 by introducing essential notions in classical information theory, such as probability distributions and classical channels. In Section 2.2, we move to the basic concepts of quantum information theory, which concerns properties of quantum states and their evolution. In Section 2.3, we introduce a variety of single-shot entropic quantities. In Section 2.4, we define majorization and see its relation to stochastic channels.

2.1. CLASSICAL PROBABILITY AND INFORMATION THEORY

Classical information theory is based on the fundamentals of (discrete) probability theory, which we briefly introduce here.

RANDOM VARIABLES AND PROBABILITY DISTRIBUTIONS

Let X[1] be a discrete random variable with some alphabet $\mathscr{X}$. Each element $x \in \mathscr{X}$, can be associated a probability $p_X(x) = \Pr\{X = x, x \in \mathscr{X}\}$, which is a real number $\mathbb{R}$ between 0 and 1, i.e. $p_X(x) \in [0,1]$. If the size of the alphabet $|\mathscr{X}| = n$, then the *probability distribution* $\{p_X(x)\}_{x\in\mathscr{X}}$ can be represented by a normalized vector $p_X = (p_1, \cdots, p_n) \in \mathbb{R}^n_{\geq 0}$, i.e. $p_i \geq 0\ \forall i$, and $\sum_{i=1}^n p_i = 1$. We denote the set of n-dimensional probability vectors as

$$V(n) = \left\{ p \in \mathbb{R}^n_{\geq 0} \;\middle|\; \sum_{i=1}^n p_i = 1 \right\}. \tag{2.1.1}$$

Classical information can be described as random variables: intuitively, since a random variable X describes uncertainty over what an actual variable is (spread across an alphabet $\mathscr{X}$), then by acquiring X, knowing what it is, we obtain some information.

How is information transmitted? Physically, it is encoded in a physical system, for example a piece of paper, or an electronic signal. This physical system carries the information from one place to another, and by observing this system, we readout the information. Given some information described by X, the amount of signals required to safely transmit it depends on p_X. For example, if p_X is spread out across all elements of $\mathscr{X}$, many signals are required for the receiver to accurately obtain X. On the other hand, if p_X is concentrated only on a small subset of values $x \in \mathscr{X}$, then the data can be *compressed* into a much smaller number of signals. A central quantity in information theory is the Shannon entropy, which carries a significant operational meaning in data compression, in the asymptotically infinite limit of idependently and identically distributed (i.i.d.) variables [46].

Definition 2.1. *Given any random variable X with a probability distribution $p_X \in V(n)$, the **Shannon entropy** is defined as* [a]

$$H(X) = H(p_X) := \sum_{i=1}^n p_i \ln \frac{1}{p_i}. \tag{2.1.2}$$

[a] Conventionally in information theory, entropic quantities are defined with logarithm base 2, in order to

[1] We adapt the convention of using the symbols X, Y, Z to denote classical random variables, and the symbols p, q, r etc. to denote probability distributions.

quantify the entropy according to the number of bits, since computational tasks deal usually with binary operations. However, we have defined all entropic quantities in this thesis with the natural logarithm instead, which is closer to the convention of statistical physics. Such a definition only differs from the conventional definition of information theory by a multiplicative factor.

Note that for all n-dimensional distributions p ,

$$0 \leq H(p) \leq \ln n, \tag{2.1.3}$$

where $H(p) = 0$ iff for a specific index $i \in \{1,n\}$, $p_i = 1$ and otherwise $\forall\, j \neq i$, $p_j = 0$. On the other hand, $H(p) = \ln n$ iff $\forall i \in \{1,n\}$, $p_i = \frac{1}{n}$ is the uniform distribution.

A special case of Shannon entropy is when $p = (p_1, p_2) \in V(2)$. The Shannon entropy in this case depends on a single variable, and is referred to as the **binary entropy**,

$$H(p) = \mathrm{h}_2(p_1) := -p_1 \ln p_1 - (1-p_1)\ln(1-p_1). \tag{2.1.4}$$

The Shannon entropy is an example of a multi-variable function, i.e. it is a function acting on p (consisting n distinct variables), and assigning a single real-value output. We may denote such functions as $f : \mathbb{R}^n \to \mathbb{R}$. Further on in this thesis, we frequently analyze these multi-variable functions in a particular limit, for example in the limit where one of the input variables go to zero. This prompts the usage of order functions denoted as $\Theta(x)$ [47], which denotes the growth of a function in such a limit.

Definition 2.2. *Consider two real-valued functions $P(x), Q(x)$. We say that $P(x) = \Theta(Q(x))$ in the limit $x \to a$ iff there exists $c_1, c_2 > 0$ and $\delta > 0$ such that for all $|x-a| \leq \delta$, $c_1 \leq \left|\frac{P(x)}{Q(x)}\right| \leq c_2$. When the limit of $x \to a$ is unspecified, by default we take $a = 0$.*

We also list a few useful properties of these functions here for $x \to 0$:
a) For any $c \neq 0$, $\Theta(c \cdot P(x)) = \Theta(P(x))$.
b) For any functions $P_1(x)$ and $P_2(x)$, $\Theta(P_1(x)) + \Theta(P_2(x)) = \Theta\left(\max\left\{|P_1(x)|, |P_2(x)|\right\}\right)$.
c) For any functions $P_1(x)$ and $P_2(x)$, $\Theta(P_1(x)) \cdot \Theta(P_2(x)) = \Theta(P_1(x)P_2(x))$.
d) For any functions $P_1(x)$ and $P_2(x)$, $\Theta(P_1(x)) / \Theta(P_2(x)) = \Theta(P_1(x)/P_2(x))$.

Example 2.1. *Consider the binary entropy as defined in Eq. (2.1.4). Then, for values of $x \ll 1$, $\mathrm{h}_2(x)$ is of order $\mathrm{h}_2(x) = -x\ln x + \Theta(x)$, which can also be written as $\mathrm{h}_2(x) = \Theta(x \ln x)$.*

CLASSICAL CHANNELS

When information is encoded in a physical system and transferred from one place to another, due to interactions with the environment, it is common that the physical system undergoes some change. As a result, the initial information X might now be described by a different random variable Y instead. Such a transmission process is often referred to as a *channel*. In other words, channels are used in information theory to model how a piece of information may be altered during transmission, due to the presence of noise.

Definition 2.3. *A **classical channel** $C : \mathscr{X} \to \mathscr{Y}$ takes symbols $x \in \mathscr{X}$ and maps them to symbols in $y \in \mathscr{Y}$ according to a conditional distribution $p_{Y|X}(y|x)$. For $|\mathscr{X}| = n$ and $|\mathscr{Y}| = m$, the channel C can be represented by a linear operator $\Lambda : V(n) \to V(m)$, which is an $m \times n$ matrix Λ where $\Lambda p_X = p_Y$. Such a matrix A is also called a **stochastic matrix**, and satisfies the following properties:*

1. *Each element is postive, i.e. for all* $i \in \{1,m\}$ *and* $j \in \{1,n\}$, $\Lambda_{ij} \geq 0$.
2. *Each column sums up to 1, i.e.* $\sum_{i=1}^{m} \Lambda_{ij} = 1, \forall\, j \in \{1,n\}$.

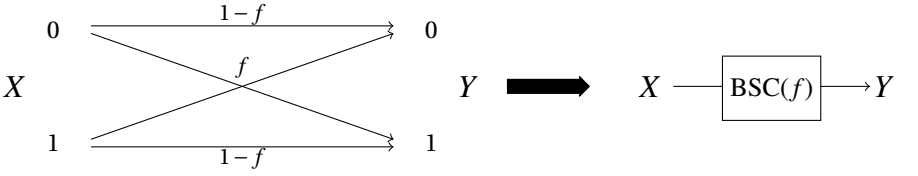

Figure 2.1: Example of a classical channel C that brings X to Y, where $\mathscr{X} = \mathscr{Y} = \{0,1\}$. This particular channel is also called a binary symmetric channel (BSC) , where a symbol gets flipped with probability f.

Figure 2.1 gives an example of a classical channel, known as the binary symmetric channel (BSC). The matrix representation of such a channel is

$$\Lambda_{BSC} = \begin{pmatrix} 1-f & f \\ f & 1-f \end{pmatrix}. \tag{2.1.5}$$

A special type of channel is a bistochastic channel, which is represented by a bistochastic matrix as defined below:

Definition 2.4 (Bistochastic matrix)**.** *An* $n \times n$ *matrix* A *is bistochastic iff:*

1. *All matrix elements are non-negative* $A_{ij} \geq 0,\ \forall 1 \leq i,j \leq n$.
2. *The sum of each column is 1, i.e.* $\sum_{i=1}^{n} A_{ij} = 1,\ \forall 1 \leq j \leq n$.
3. *The sum of each row is 1, i.e.* $\sum_{j=1}^{n} A_{ij} = 1,\ \forall 1 \leq i \leq n$.

By definition, the matrix A *is bistochastic iff it represents a classical channel that preserves the maximally mixed distribution* $\eta = \{\frac{1}{n}, \cdots, \frac{1}{n}\}$, *i.e.* $A\eta = \eta$.

2.2. QUANTUM INFORMATION THEORY

This section aims to give the reader a brief overview of the tools and framework from quantum information theory, in which the results within this thesis is formulated. We assume that the reader is familiar with basic concepts from linear algebra. For a detailed introduction to quantum information theory, the reader is referred to the classic textbook by Nielsen and Chuang [48], and the lecture notes by Mark Wilde on quantum Shannon theory [49].

2.2.1. QUANTUM STATES AND EVOLUTION

We begin with one of the basic postulates in quantum theory, which concerns the Hilbert space that represents any quantum system[2].

[2]We adapt the convention of using symbols such as A, B, C to denote quantum systems.

Box 2.2.1: State space/Hilbert space

Postulate 1. *Associated to any physical system A is a complex vector space with inner product, that is known as the **state space**, or **Hilbert space** of the system, commonly denoted as $\mathcal{H}_A$. The system can be completely described by its state vector, which is a unit vector in $\mathcal{H}_A$.*

According to standard convention in quantum mechanics [48], we use the *bra-ket* notations to denote vectors in $\mathcal{H}$ by a "ket", for example $|\psi\rangle \in \mathcal{H}$. The "bra" vectors are dual vectors denoted as $\langle\psi| \in \mathcal{H}^*$, where $\mathcal{H}^*$ is the dual space of $\mathcal{H}$. If a quantum state is represented by a state vector, it means that full information of the state is already known. However, to further incorporate classical uncertainty into the notation for quantum states, the density matrix formalism is often used.

Before defining the density matrix, we first recall that given any two Hilbert spaces $\mathcal{H}$ and $\mathcal{H}'$, linear operators L are mappings $L : \mathcal{H} \to \mathcal{H}'$ such that addition and scalar multiplication are preserved. Such linear operators are represented by a $d' \times d$ matrix, where d, d' are dimensions of $\mathcal{H}, \mathcal{H}'$ respectively. We now recall several types of common linear operators $L : \mathcal{H} \to \mathcal{H}$ for a certain Hilbert space $\mathcal{H}$.

Definition 2.5. *Given any Hilbert space $\mathcal{H}$, the set of **Hermitian operators** $\mathrm{Herm}(\mathcal{H})$ is the set of linear operators that are self-adjoint, i.e.*

$$\mathrm{Herm}(\mathcal{H}) := \left\{ L : \mathcal{H} \to \mathcal{H} \;\middle|\; L^\dagger = L \right\}. \tag{2.2.1}$$

Any Hermitian operator $H \in \mathrm{Herm}(\mathcal{H})$ must have real-valued eigenvalues.

Definition 2.6. *Given any Hilbert space $\mathcal{H}$, the set of **positive semi-definite operators** $\mathrm{Pos}(\mathcal{H})$ is given by*

$$\mathrm{Pos}(\mathcal{H}) := \{ L \in \mathrm{Herm}(\mathcal{H}) \mid L \geq 0 \}, \tag{2.2.2}$$

where the notation $L \geq 0$ indicates that L is a non-negative operator, i.e. each of its eigenvalues are non-negative.

A valid quantum state can be represented by a density matrix ρ[3], which is a special type of positive demi-definite operator as defined below:

Definition 2.7. *Given any Hilbert space $\mathcal{H}$, the set of **quantum states** (or density matrices) on $\mathcal{H}$ is given by*

$$S(\mathcal{H}) := \left\{ \rho \in \mathrm{Pos}(\mathcal{H}) \mid \mathrm{tr}(\rho) = 1 \right\}, \tag{2.2.3}$$

where the trace $\mathrm{tr}(\rho) = \sum_i \rho_{ii}$ denotes the sum of diagonal elements.

A simple example of a density matrix is given by the *maximally mixed state*.

[3]Throughout this thesis we adapt the convention of using symbols such as ρ, σ, ω to denote density matrices.

Definition 2.8. *Given any quantum system A corresponding to some Hilbert space $\mathcal{H}_A$ of dimension d_A, the maximally mixed state is given by*

$$\pi_A = \frac{1}{d_A}\sum_{i=1}^{d_A} |i\rangle\langle i|_A = \frac{1}{d_A}\mathbb{1}_A, \tag{2.2.4}$$

where $\{|i\rangle_A\}_i$ is the standard basis, i.e.

$$|i\rangle_A = (0 \ \cdots \ \underbrace{1}_{\text{i-th position}} \ \cdots \ 0)^T. \tag{2.2.5}$$

The matrix $\mathbb{1}_A$ is simply the identity operator. Since $\mathbb{1}_A$ is invariant under all basis transformations, the maximally mixed state has the same form when written in any basis, i.e. for any orthonormal basis $\{|e_i\rangle_A\}_i$, $\pi_A = \frac{1}{d_A}\sum_{i=1}^{d_A} |e_i\rangle\langle e_i|_A$.

COMPOSITE QUANTUM SYSTEMS

Given two quantum systems A, B with their respective Hilbert spaces $\mathcal{H}_A, \mathcal{H}_B$, the joint system is commonly denoted as AB, and the joint Hilbert space is simply the tensor product of individual Hilbert spaces $\mathcal{H}_{AB} = \mathcal{H}_A \otimes \mathcal{H}_B$. There is an easy way to construct a basis for this joint system: for any complete, orthonormal bases $\{|e_i\rangle_A\}_{i=1}^{d_A}$ and $\{|f_j\rangle_B\}_{j=1}^{d_B}$ for the individual systems A and B,

$$\left\{ \{ |e_i\rangle_A \otimes |f_j\rangle_B \}_{i=1}^{d_A} \right\}_{j=1}^{d_B} \tag{2.2.6}$$

is a complete orthonormal basis for $\mathcal{H}_{AB}$.

Consider the case where the systems A and B were prepared independently from each other in states ρ_A, ρ_B, then the joint state $\rho_{AB} = \rho_A \otimes \rho_B$ is simply given by the tensor product of these states. If ρ_{AB} is of tensor product form, then it implies that there are no correlations between system A and B.

HOW QUANTUM STATES EVOLVE WITH TIME

The second postulate concerns the natural evolution of an isolated quantum system (i.e. a system that does not interact with anything else).

Box 2.2.2: Evolution of a quantum system

Postulate 2. *The time evolution of a quantum state $\rho \in \mathcal{H}$ is described by the Schrödinger equation. Suppose that at $t = 0$, the system is in the quantum state ρ_0. The quantum state after some time t is then given by*

$$\rho_t = U_t \rho_0 U_t^\dagger, \tag{2.2.7}$$

*where $U_t = e^{-i\hat{H}t}$, and $\hat{H} \in \mathrm{Herm}(\mathcal{H})$ is an operator called the **Hamiltonian** associated with the system.*

Remark 2.1. *For any real-valued $t \geq 0$, operator U_t is also Hermitian, and it is a **unitary operator**, i.e. U_t has the property that $U_t U_t^\dagger = U_t^\dagger U_t = \mathbb{1}$ is the identity operator.*

Since the Hamiltonian is a Hermitian operator, by the Spectral Decomposition Theorem (Box 2.2, [48]) it can be diagonalized, i. e. one can always write $\hat{H}$ as

$$\hat{H} = \sum_i E_i \Pi_{E_i}, \tag{2.2.8}$$

with eigenvalues E_i, and a complete set of orthogonal projectors Π_{E_i}[4]. Given the unique physical meaning of the system's Hamiltonian, by default we write a quantum state ρ in the basis of its Hamiltonian $\hat{H}$, and call the state ρ *block-diagonal* if ρ and $\hat{H}$ are simultaneously diagonalizable, i.e. there exists an ordered eigenbasis of the Hamiltonian, such that ρ is diagonal in this basis[5]. When necessary, we also use the notation $(\rho, \hat{H})$ in order to refer to the state together with its Hamiltonian as a **state-Hamiltonian pair**.

A block-diagonal density matrix ρ_0 always commutes with its Hamiltonian, i.e. $[\rho_0, \hat{H}] = 0$. Therefore, according to Postulate 2, if ρ_0 commutes with the Hamiltonian, then in fact when left isolated from the rest of the world, it remains unchanged with respect to time. This is seen by Eq. (2.2.7), since $[\rho_0, \hat{H}] = 0$, for any $t \geq 0$, we have that $[\rho_0, U_t] = 0$ holds as well, and therefore

$$\rho_1 = U_t \rho_0 U_t^\dagger = \rho_0 U_t U_t^\dagger = \rho_0. \tag{2.2.9}$$

A state $\rho \in \mathscr{H}$ is **pure** if $\text{rank}(\rho) = 1$, and ρ can be written as $\rho = |\psi\rangle\langle\psi|$ where $|\psi\rangle$ is a normalized vector in $\mathscr{H}$. In general, since the density matrix is a positive semi-definite operator, again by spectral decomposition it can always be diagonalized in some basis:

$$\rho = \sum_i \mu_i |e_i\rangle\langle e_i|. \tag{2.2.10}$$

If we have a function $f : \mathbb{R} \to \mathbb{R}$, then $f(\rho)$ is used to denote

$$f(\rho) = \sum_i f(\mu_i) |e_i\rangle\langle e_i|. \tag{2.2.11}$$

Throughout this thesis, we will encounter a particular quantum state called the *thermal state*, or known also as the Gibbs state, which we denote as τ throughout the thesis.

Definition 2.9. *Consider a quantum system described by the Hamiltonian $\hat{H}$. Then given any real-valued parameter $\beta \geq 0$, the **thermal/Gibbs state** at inverse temperature β is given by a block-diagonal state:*

$$\tau^\beta = \frac{e^{-\beta \hat{H}}}{Z^\beta}, \tag{2.2.12}$$

*where $Z^\beta = \text{tr}\left(e^{-\beta \hat{H}}\right)$ is known as the **partition function** of the system (one may also view it as the normalization factor for the thermal state).*

[4] A projector P is a linear operator such that $P^2 = P$. A projector is orthogonal if its rows and columns consist of linearly independent vectors.

[5] For the case where $\hat{H}$ is fully non-degenerate, it has a unique eigenbasis, therefore a state ρ_0 that commutes with $\hat{H}$ is automatically block-diagonal. However, if $\hat{H}$ has degenerate eigenvalues, then it does not have a unique eigenbasis. Therefore, $[\rho_0, \hat{H}] = 0$ does not necessarily imply anymore that ρ_0 is diagonal in any eigenbasis of $\hat{H}$; it only implies the existence of such a common eigenbasis.

In classical equilibrium thermodynamics, the partition function is a central quantity of interest, since it contains information about both the temperature and Hamiltonian of the system. We shall discuss this Gibbs state in more detail later in Chapters 3 and 4. Many important macroscopic variables of a thermodynamical system, such as the total energy, entropy etc may be expressed in terms of Z^β (or with its derivative with respect to β) [2].

2.2.2. QUANTUM CHANNELS

We have seen in Section 2.1 how a classical channel maps a probability distribution to another. Analogous to the classical case, a generic evolution/process that a quantum state undergoes can be viewed as an action of a **quantum channel** on the state. Mathematically, a quantum channel $\mathcal{N}_{A\to B} : S(\mathcal{H}_A) \to S(\mathcal{H}_B)$ is a linear map that takes a density matrix $\rho_A \in S(\mathcal{H}_A)$ to another density matrix in $S(\mathcal{H}_B)$. If $\mathcal{H}_A = \mathcal{H}_B$, then we write the channel simply as $\mathcal{N}_A$.

Let us consider what are the requirements for a linear map $\mathcal{N}_{A\to B}$ to be a valid quantum channel. Since $\mathcal{N}_{A\to B}(\rho_A)$ is also a quantum state, this means that the linear map $\mathcal{N}_{A\to B}$ has to satisfy the following property:

- Trace Preserving: $\mathrm{tr}(\mathcal{N}_{A\to B}(\rho_A)) = \mathrm{tr}(\rho_A)$.

On the other hand, one might imagine the channel acting only upon A, while A is part of a larger composite system AE. Then for $\mathcal{N}_{A\to B}$ to produce a valid final quantum state, we must have that for any additional quantum system E, and state $\rho_{AE} \in \mathcal{H}_{AE}$:

- Complete Positivity: $(\mathcal{N}_{A\to B} \otimes \mathbb{1}_E)(\rho_{AE}) \geq 0$.

Definition 2.10. *Consider quantum systems A and B. Then a quantum channel from A to B, $\mathcal{N}_{A\to B} : S(\mathcal{H}_A) \to S(\mathcal{H}_B)$ is a linear map which is completely positive (CP) and trace preserving (TP), also referred to as a completely positive trace preserving map (CPTPM).*

An example of a quantum channel is the *partial trace*, which acts on a quantum system by effectively discarding a subsystem, ending up with what is called the *reduced state*.

Definition 2.11. *Consider a quantum state $\rho_{AB} \in S(\mathcal{H}_{AB})$ of a composite system AB, which for any orthonormal basis sets $\{|e_i\rangle_A\}_i$ and $\{|f_k\rangle_B\}_k$, can be written as*

$$\rho_{AB} = \sum_{ijkl} \lambda_{ij}^{kl} |e_i\rangle\langle e_j|_A \otimes |f_k\rangle\langle f_l|_B. \tag{2.2.13}$$

The partial trace operation over B, denoted as $\mathrm{tr}_B : S(\mathcal{H}_{AB}) \to S(\mathcal{H}_B)$ gives

$$\rho_A = \mathrm{tr}_B(\rho_{AB}) := \sum_{ijkl} \lambda_{ij}^{kl} |e_i\rangle\langle e_j|_A \otimes \mathrm{tr}(|f_k\rangle\langle f_l|_B) = \sum_{ij} \nu_{ij} |e_i\rangle\langle e_j|_A, \tag{2.2.14}$$

where $\nu_{ij} = \sum_k \lambda_{ij}^{kk}$, and ρ_A is called the reduced state of system A.

2.2.3. DISTANCE MEASURES

Given two quantum states $\rho, \sigma \in S(\mathcal{H})$ in a particular Hilbert space, or two probability vectors $p, q \in V(k)$ on a k-dimensional probability space, how hard is it to distinguish them? There are a few well-known quantities which quantifies the distance between two (either classical or quantum) states. We introduce two here: trace distance, and fidelity.

TRACE DISTANCE

One of the most commonly used distance quantity is the **trace distance**, as defined in Def. 2.12. More commonly, the term "statistical distance" is used for quantifying the distance between two classical probability distributions. However, since in this thesis we frequently consider quantum states ρ, σ that share a common eigenbasis, the trace distance between ρ and σ reduces to the statistical distance between their eigenvalues. Therefore, we combine both notations.

Definition 2.12. *The trace distance $d(p,q)$ between two probability distributions $p, q \in V(n)$ is given by*

$$d(p,q) := \frac{1}{2}\sum_{i=1}^{n} |p_i - q_i| = \sum_{j \in S} p_j - q_j, \tag{2.2.15}$$

where $S = \{j \,|\, p_j \geq q_j\}$ denotes the set of indices j where $p_j \geq q_j$. Similarly, the trace distance between two quantum states ρ, σ is

$$d(\rho,\sigma) := \frac{1}{2}\mathrm{tr}|\rho - \sigma|, \tag{2.2.16}$$

where for any matrix A, $|A| = \sqrt{A^\dagger A}$.

Note that when ρ and σ commute, then if we denote $p = \mathrm{eig}(\rho)$ and $q = \mathrm{eig}(\sigma)$ to be the vector containing eigenvalues of states ρ, σ respectively (corresponding to the same ordered basis), then $d(\rho,\sigma) = d(p,q)$. We say that two quantum states ρ and σ, or two distributions p, q are ε-close to each other, if $d(\rho,\sigma) \leq \varepsilon$ or $d(p,q) \leq \varepsilon$.

The trace distance is a *metric*, which means that for any distributions p, q, and r, it satisfies the following properties:

1. Symmetric: $d(p,q) = d(q,p)$.
2. Non-negativity: $d(p,q) \geq 0$ with equality iff $p = q$.
3. Triangle inequality: $d(p,q) + d(q,r) \geq d(p,r)$.

The trace distance also satisfies an important property known as the **data processing inequality**, namely that for any CPTPM $\mathcal{N}$, and any quantum states ρ, σ,

$$d(\mathcal{N}(\rho), \mathcal{N}(\sigma)) \leq d(\rho,\sigma). \tag{2.2.17}$$

Physically speaking, it means that the distinguishability of two quantum states can never increase through a quantum channel.

The trace distance between two states ρ and σ can also be written as

$$d(\rho,\sigma) = \max_{0\leq M\leq \mathbb{1}} \mathrm{tr}\left[M\left(\rho-\sigma\right)\right] . \tag{2.2.18}$$

This implies that the trace distance enjoys an appealing operational interpretation: being ε-close in trace distance means that if we were given states ρ and σ (or random variables according to distributions p,q) with probability $1/2$ each, then our probability of correctly distinguishing them by any physically allowed measurement is upper bounded by $1/2+\varepsilon/2$ [48]. In other words, being close in the trace distance means that the two states cannot be distinguished well by any conceivable physical process.

FIDELITY

Another common measure for closeness of states is known as the **fidelity**, which for pure states is directly related to their inner product.

Definition 2.13. *Given density matrices ρ and σ, the* fidelity *between ρ and σ is*

$$F(\rho,\sigma) = \mathrm{tr}\left[\sqrt{\sqrt{\rho}\sigma\sqrt{\rho}}\right] . \tag{2.2.19}$$

For pure states $\rho = |\Psi_1\rangle\langle\Psi_1|$ and $\sigma = |\Psi_2\rangle\langle\Psi_2|$ the fidelity takes on a simplified form:

$$F(\rho,\sigma) = |\langle\Psi_1|\Psi_2\rangle| . \tag{2.2.20}$$

For any two quantum states ρ,σ, the fidelity satisfies the following properties

1. Between 0 and 1: $0 \leq F(\rho,\sigma) \leq 1$.
2. Symmetric: $F(\rho,\sigma) = F(\sigma,\rho)$.
3. Multiplicative under tensor product: $F(\rho_1\otimes\rho_2,\sigma_1\otimes\sigma_2) = F(\rho_1,\sigma_1)\cdot F(\rho_2,\sigma_2)$.
4. Invariant under unitary operations: $F(\rho,\sigma) = F(U\rho U^\dagger, U\sigma U^\dagger)$.
5. Monotonically increasing under CPTPMs (data processing): for any CPTPM $\mathcal{N}$, $F(\mathcal{N}(\rho),\mathcal{N}(\sigma)) \geq F(\rho,\sigma)$.
6. Relation to trace distance: for any quantum states ρ,σ, we have that $1-F(\rho,\sigma) \leq d(\rho,\sigma) \leq \sqrt{1-F^2(\rho,\sigma)}$. Conversely, we also have that $1-d(\rho,\sigma) \leq F(\rho,\sigma) \leq \sqrt{1-d^2(\rho,\sigma)}$. This is known as the Fuchs-van de Graaf inequality [50].

2.2.4. ENTROPIC QUANTITIES

Given any state (be it a classical random variable or a quantum state), entropic functions are functions that map the state to a real-valued parameter, and these functions satisfy certain properties that intuitively provide a quantification of how much information is contained in the state. Two commonly used entropic quantities are introduced here: the von Neumann entropy and the relative entropy.

VON NEUMANN ENTROPY

A central quantity that measures the amount of disorderness in a quantum state is given by the von Neumann entropy, which is a direct generalization of the Shannon entropy.

Definition 2.14. *Given any quantum system A in some state ρ_A, the* ***von Neumann entropy*** *of the state is defined as*

$$S(A) = S(\rho_A) := -\operatorname{tr}(\rho \ln \rho). \tag{2.2.21}$$

Let us consider the vector $p = \operatorname{eig}(\rho_A)$. Then we see from Eq. (2.2.11) that $S(\rho_A) = H(p)$ is precisely the Shannon entropy. Similarly as in the classical case of the Shannon entropy, if $\dim(A) = n$, then for any state ρ_A, the von Neumann entropy $0 \leq S(\rho_A) \leq \ln n$ where equality $S(\rho_A) = 0$ is achieved when $\rho_A = |\psi\rangle\langle\psi|_A$ is pure. On the other hand, $S(\rho_A) = \ln n$ is achieved only for the maximally mixed state of dimension n, $\rho_A = \pi_A$.

The difference between von Neumann entropy of two states can also be upper bounded by a function of the trace distance.

Theorem 2.1 (Fannes inequality [51])**.** *For any two density matrices ρ, σ of dimension n, let $t = d(\rho, \sigma)$ be the trace distance between the two quantum states. Then*

$$\left|S(\rho) - S(\sigma)\right| \leq t \cdot \ln(n-1) + h_2(t). \tag{2.2.22}$$

The von Neumann entropy has been studied extensively in quantum information theory, and we briefly list some useful properties here. For any quantum states ρ, σ,

1. Non-negativity: $S(\rho) \geq 0$.
2. Continuity: Fannes inequality, see Theorem 2.1.
3. Additivity under tensor product: $S(\rho \otimes \sigma) = S(\rho) + S(\sigma)$.
4. Invariance under isometries: $S(U\rho U^\dagger) = S(\rho)$.
5. Subadditivity: for any two quantum systems A, B described by a joint state ρ_{AB},

$$S(A) + S(B) \geq S(AB). \tag{2.2.23}$$

In fact, the von Neumann entropy (up to a constant) is proven to be the unique function on density matrices satisfying the above 5 properties [52]. It also satisfies a useful property:

6. Concavity: for any probability distribution p, and mixture of states $\rho' = \sum_i p_i \rho_i$,

$$S(\rho') \geq \sum_i p_i S(\rho_i).$$

RELATIVE ENTROPY

Another quantity, the **quantum relative entropy**, provides a non-symmetric measure of closeness between two states. Like its classical counterpart, which we will see later, besides being an important quantity by itself [53], it is also a parent quantity that generates other entropic measures, such as both the unconditional and conditional von Neumann entropy, mutual information (Chapter 11, [49]).

Definition 2.15. *For two quantum states ρ, σ, the relative entropy of ρ to σ is given by*

$$D(\rho\|\sigma) := \mathrm{tr}(\rho \ln \rho) - \mathrm{tr}(\rho \ln \sigma). \tag{2.2.24}$$

In the case where ρ, σ are diagonal in the same (ordered) basis, with p, q denoting the respective eigenvalue vectors of ρ, σ, then

$$D(\rho\|\sigma) = D(p\|q) := \sum_i p_i \ln \frac{p_i}{q_i}, \tag{2.2.25}$$

which is the classical version of $D(\rho\|\sigma)$, known as the Kullback-Leibler divergence.

For any quantum states, the relative entropy satisfies the following properties:

1. Non-negativity: $D(\rho\|\sigma) \geq 0$, with equality iff $\rho = \sigma$.
2. Additivity under tensor product: $D(\rho_1 \otimes \rho_2\|\sigma_1 \otimes \sigma_2) = D(\rho_1\|\sigma_1) + D(\rho_2\|\sigma_2)$.
3. Invariance under unitaries: $D(\rho\|\sigma) = D(U\rho U^\dagger\|U\sigma U^\dagger)$.
4. Data processing: for any quantum channel $\mathcal{N}$, $D(\rho\|\sigma) \geq D(\mathcal{N}(\rho)\|\mathcal{N}(\sigma))$.

2.3. INFORMATION-THEORETIC SINGLE-SHOT QUANTITIES

We have earlier seen the Shannon entropy, and its quantum counterpart (von Neumann entropy). These quantities have significant operational meaning when dealing with i.i.d. variables, especially in the limit of infinitely many such variables. However, in most real-world information processing tasks, we deal with only a finite amount of data, and furthermore it is not always possible to assume no inter-correlation at all between distinct pieces of data. Nevertheless, in such cases it is still desirable to analyze tasks (for example the safe recovery of compressed data), by understanding the single-shot probability of success, i.e. for a single attempt at the task of interest.

For this reason, generalizations of the relative entropy and von Neumann entropy have been developed. These quantities are called Rényi divergences and entropies, named after the Hungarian mathematician Alfred Rényi, and are widely used in information theory, especially when one is concerned with tasks such as randomness extraction [54–56], source coding [54, 57], or hypothesis testing [58, 59] for finite block lengths (instead of the asymptotically infinite limit).

2.3.1. RÉNYI DIVERGENCES

The Rényi divergences are a generalization of the relative entropy for two states/distributions.

Definition 2.16 (Classical Rényi divergences). *Consider any two probability distributions $p, q \in V(n)$. The classical Rényi divergences are defined for $\alpha \in [-\infty, \infty]$:*

$$D_\alpha(p\|q) := \frac{\mathrm{sgn}(\alpha)}{\alpha - 1} \cdot \ln \sum_{i=1}^{n} p_i^\alpha q_i^{1-\alpha}, \tag{2.3.1}$$

where $\mathrm{sgn}(\alpha)$ is the signum function, i.e. $\mathrm{sgn}(\alpha) = 1$ if $\alpha \geq 0$, and $\mathrm{sgn}(\alpha) = -1$ otherwise. The cases $\alpha = \{0, 1, \infty, -\infty\}$ are defined via the suitable limit, namely

$$D_0(p\|q) := \lim_{\alpha\to 0^+} D_\alpha(p\|q) = -\ln \sum_{i:p_i\neq 0}^{n} q_i, \tag{2.3.2}$$

$$D_1(p\|q) := \lim_{\alpha\to 1} D_\alpha(p\|q) = \sum_{i}^{n} p_i(\ln p_i - \ln q_i) = D(p\|q), \tag{2.3.3}$$

$$D_\infty(p\|q) := \lim_{\alpha\to\infty} D_\alpha(p\|q) = \ln \max_i \frac{p_i}{q_i}, \tag{2.3.4}$$

$$D_{-\infty}(p\|q) := -\lim_{\alpha\to-\infty} D_\alpha(p\|q) = D_\infty(q\|p), \tag{2.3.5}$$

For two quantum states ρ,σ which are simultaneously diagonalizable, i.e. they commute with each other, we write

$$D_\alpha(\rho\|\sigma) := D_\alpha(\mathrm{eig}(\rho)\|\mathrm{eig}(\sigma)). \tag{2.3.6}$$

Since Eq. (2.3.3) holds, when $\alpha\to 1$ the Rényi divergence coincides with the relative entropy as defined in Eq. (2.2.25), we always write D_1 simply as D.

There exists a useful relation between two Rényi divergences for $\alpha\notin\{0,1\}$:

$$\alpha\cdot\mathrm{sgn}(1-\alpha)\cdot D_{1-\alpha}(p||q) = (1-\alpha)\cdot\mathrm{sgn}(\alpha)\cdot D_\alpha(q||p). \tag{2.3.7}$$

For some important properties of Rényi divergences, the reader can refer to [60, 61]. In most literature, the Rényi divergence is only defined for only non-negative $\alpha\geq 0$; however for our purposes we will define them for all negative α as well. The divergences D_α in Def. 2.16 satisfy data processing inequality for all $\alpha\in[-\infty,\infty]$: for any stochastic map Λ,

$$D_\alpha(\Lambda(p)\|\Lambda(q)) \leq D_\alpha(p\|q). \tag{2.3.8}$$

The range $\alpha\in[0,\infty]$ is proven in [61], while the negative regime is an immediate consequence of Eq. (2.3.7).

For any distributions p,q, the Rényi divergence is non-decreasing in $\alpha\in[0,\infty]$:

$$D_\alpha(p\|q)\leq D_\gamma(p\|q) \tag{2.3.9}$$

for $\alpha\leq\gamma$ (see Theorem 3 of Ref. [60]).

QUANTUM RÉNYI DIVERGENCES

For general quantum states ρ,σ which do not commute with each other, several generalized versions of the Rényi divergences have also been defined in order to capture the non-commutativity of quantum states. Due to this non-commutativity, the Rényi divergence can be extended for quantum states in many different ways (see e.g. [62, 63]) such that it reduces to the classical Rényi divergences when states commute.

The most straightforward generalization is the following candidate for $\alpha\in(0,1)\cup(1,\infty)$:

$$\tilde{D}_\alpha(\rho||\sigma) := \frac{\mathrm{sgn}(\alpha)}{\alpha-1}\cdot\ln\left[\mathrm{tr}\left(\rho^\alpha\sigma^{1-\alpha}\right)\right], \tag{2.3.10}$$

and $\tilde{D}_0,\tilde{D}_1,\tilde{D}_\infty$ are defined by limits. For $\alpha\to 1$, the quantum relative entropy is recovered:

$$\lim_{\alpha\to 1^+}\tilde{D}_\alpha(\rho||\sigma) = \mathrm{tr}(\rho\ln\rho-\rho\ln\sigma) = D(\rho||\sigma). \tag{2.3.11}$$

As proven in Lemma B.4 of [64], a subset of these Rényi divergences are known to be monotonic under CPTPMs:

$$\tilde{D}_\alpha(\mathcal{N}(\rho)||\mathcal{N}(\sigma)) \leq \tilde{D}_\alpha(\rho||\sigma), \qquad \alpha \in [0,2]. \tag{2.3.12}$$

Another version of the quantum Rényi divergence was more recently established, sometimes referred to as the "sandwiched" Rényi divergences (due to its form in Eq. (2.3.13)). The motivation for defining such a quantity is that it has the advantage of being compatible with conditional entropic quantities, but we will omit the discussion here, and provide directly its definition and properties.

Definition 2.17 (**Quantum Rényi divergences** [65, 66])**.** *Given arbitrary quantum states $\rho, \sigma \in S(\mathcal{H})$, then for $\alpha \in [0,\infty]$, the Rényi divergence of ρ relative to σ is defined as*

$$\hat{D}_\alpha(\rho\|\sigma) := \frac{1}{\alpha-1}\ln\left[\mathrm{tr}\left(\rho^{\frac{1-\alpha}{2\alpha}}\sigma\rho^{\frac{1-\alpha}{2\alpha}}\right)^\alpha\right] \tag{2.3.13}$$

For ρ, σ diagonal in the same ordered basis, let $p = \mathrm{eig}(\rho)$ and $q = \mathrm{eig}(\sigma)$ respectively. Then the Rényi divergences reduce to the classical form $\hat{D}_\alpha(\rho\|\sigma) = D_\alpha(p\|q)$.

The cases $\alpha = \{0,1,\infty\}$ are obtained by the respective limits, and $\hat{D}_1(\rho||\sigma)$ reduces to $D(\rho\|\sigma)$. Recently it was proven in [63] (see also [67]) that this entropy is monotonic under quantum completely positive trace preserving maps for $\alpha \geq 1/2$, namely for any CPTP map $\mathcal{N}$ and states ρ, σ, we have that:

$$\hat{D}_\alpha(\mathcal{N}(\rho)||\mathcal{N}(\sigma)) \leq \hat{D}_\alpha(\rho||\sigma), \qquad \alpha \geq 1/2. \tag{2.3.14}$$

Note again, that if ρ and σ are diagonal in the same basis, then both quantities $\tilde{D}_\alpha(\rho\|\sigma)$ and $\hat{D}_\alpha(\rho\|\sigma)$ reduce to the classical version, involving only the eigenvalues p and q.

2.3.2. RÉNYI ENTROPIES

Definition 2.18. *Given a probability distribution $p \in V(n)$, the Rényi entropies are defined for $\alpha \in \mathbb{R}\setminus\{0,1\}$ as*

$$H_\alpha(p) := \frac{\mathrm{sgn}(\alpha)}{1-\alpha}\cdot\ln\sum_{i=1}^n p_i^\alpha, \tag{2.3.15}$$

where $\mathrm{sgn}(\alpha)$ is defined in Def. 2.16. Again, for the cases of $\alpha \in \{-\infty,0,1,\infty\}$, $H_\alpha(p)$ is defined by its corresponding limits:

$$H_0(p) = \ln\ \mathrm{rank}(p), \qquad H_1(p) = -\sum_{i=1}^n p_i\ln p_i = H(p), \tag{2.3.16}$$

$$H_\infty(p) = -\ln\left(\max_i p_i\right), \qquad H_{-\infty}(p) = \ln\left(\min_i p_i\right). \tag{2.3.17}$$

For any quantum state ρ, the quantum Rényi entropy is

$$H_\alpha(\rho) := H_\alpha(\mathrm{eig}(\rho)). \tag{2.3.18}$$

The Rényi entropies can be derived from the Rényi divergences as follows: for any classical probability distribution $p = (p_1, \cdots, p_n) \in V(n)$,

$$H_\alpha(p) = \mathrm{sgn}(\alpha) \cdot \ln n - D_\alpha(p \| \eta) \ , \tag{2.3.19}$$

with $\eta = \left(\frac{1}{n}, \frac{1}{n}, ..., \frac{1}{n}\right)$ is the uniform probability distribution.

Again, it is worth noting that the Rényi entropies have generally been defined only for $\alpha \geq 0$, but we define it here for all real-valued α.

2.4. MAJORIZATION

For any real-component vector $x = (x_1, \ldots x_n) \in \mathbb{R}^n_{\geq 0}$, let $x^\downarrow$ be the vector obtained by rearranging the components of x in decreasing order: $x^\downarrow = (x^\downarrow_1, \ldots, x^\downarrow_n)$ where $x^\downarrow_1 \geq \ldots \geq x^\downarrow_n$. Majorization is a partial order, which is defined for vectors $x, y \in \mathbb{R}^n_{\geq 0}$. We say that x majorizes y, or denoted as $x \succ y$, iff for all $m = 1, \ldots n$,

$$\sum_{i=1}^{m} x^\downarrow_i \geq \sum_{i=1}^{m} y^\downarrow_i, \quad \text{and} \quad \sum_{i=1}^{n} x^\downarrow_i = \sum_{i=1}^{n} y^\downarrow_i. \tag{2.4.1}$$

Majorization is a common relation used in comparing normalized probability vectors to quantify disorder. For example, if $x \succ y$, one will see that the distribution described by y is more "spread out" compared to x. The Shannon entropy, for example, $H(y)$ would also be greater than $H(x)$.

MAJORIZATION AND UNITAL CHANNELS

We have, in the previous section, seen the case where two vectors are related to each other by majorization: for example, consider two probability vectors p, q corresponding to two random variables X and Y respectively. If $p \succ q$, then intuitively speaking, the distribution of q is more spread out compared to p. Theorem 2.2 makes this notion precise, by establishing that there exists a certain stochastic process that will bring X to Y.

Theorem 2.2 (Birkhoff-von Neumann theorem, [68, 69])**.** *For all $p, q \in \mathbb{R}^n_{\geq 0}$, the following are equivalent:*

1. *The vector p majorizes q, i.e. $p \succ q$.*
2. *There exists a bistochastic matrix A such that $Ap = q$.*

Theorem 2.2, when applied to quantum states, implies that majorization dictates the possibility of a state transition $\rho \to \sigma$ via unital maps[6]:

[6] A unital map is a CPTPM $\mathscr{E}_A$ such that the maximally mixed state is preserved, i.e. $\mathscr{E}(\pi_A) = \pi_A$.

Theorem 2.3. *Consider quantum states ρ, σ with $p = \mathrm{eig}(\rho)$ and $q = \mathrm{eig}(\sigma)$ respectively. Then there exists a unital map $\mathscr{E}$ such that $\mathscr{E}(\rho) = \sigma$ iff $p \succ q$.*

SCHUR'S THEOREM

For any $n \times n$ Hermitian matrix B, the diagonal entries of B can be related to its eigenvalues by majorization as well:

Theorem 2.4 ([70], Chapter 9, Theorem B.1.)**.** *Consider any $n \times n$ Hermitian matrix B, and let* $\mathrm{diag}(B)$ *denote the vector containing the diagonal entries of B. Then*

$$\mathrm{eig}(B) \succ \mathrm{diag}(B). \tag{2.4.2}$$

SCHUR CONVEX FUNCTIONS

A function f is called Schur convex if it always preserves the majorization order, i.e. if $x \succ y$ implies $f(x) \geq f(y)$. If the majorization order is always reversed, the function is called Schur concave. A function is called *strictly* Schur convex if $x \succ y$ implies $f(x) > f(y)$ except when $x^{\downarrow} = y^{\downarrow}$, then $f(x) = f(y)$.

A useful criterion for strict Schur convexity is stated in the following lemma:

Lemma 2.1. *Consider a function $f : R_+^k \to R$ of the form $f(x) = \sum_i g(x_i)$. Then, $f(x)$ is (strictly) Schur convex/concave if and only if $g(x)$ is (strictly) convex/concave.*

Using Lemma 2.1, and the strict concavity of the logarithm, we see that the function $\sum_i \ln p_i$ is strictly Schur concave. On the other hand, the Rényi entropies are also Schur concave functions:

Lemma 2.2. *For $\alpha \in (-\infty, \infty)$, the Rényi entropies H_α are strictly Schur concave.*

3

RESOURCE THEORIES

In this chapter, we introduce the resource theoretic framework, which is an approach used to manage any "valuable resources", such as entanglement, purity etc. Such frameworks are characterized by two main elements: a set of predefined (free) operations and states, that one assumes to be easily obtained at no cost. Given these ground rules, one can then ask: what is achievable using such free operations and states? This usually results in a set of state transition conditions, that tell us if a particular state ρ may evolve into another state ρ' via the usage of free operations and states. Here, we see how thermodynamics may be seen as a resource theory, by laying down the ground rules of free operations and states corresponding to thermodynamical interactions. We then proceed with a review of how the resource theory framework connects with other approaches in thermodynamics.

3.1. WHAT ARE RESOURCE THEORIES?

Resource theories are conceptual, information-theoretic frameworks that allow one to quantify and manage "valuables", or else called resources. Conceptually, resources are valuable because it is hard or costly to create them. Suppose an experimenter in his/her lab has a constrained ability to perform certain types of operations, then any initial state that cannot be created from such operations becomes valuable to him/her. A generic resource theory therefore is determined by two key elements:

1. a class of *free operations* that are allowed to be implemented at no cost,
2. a class of *free states* that one can generate and use at no cost[1].

Given the above operations and states that are assumed to be easily created, one can then ask: if the experimenter possesses a quantum state ρ, what are the set of states he/she can possibly reach by manipulating ρ, under the usage of these free operations and states? This produces the third aspect of resource theories, namely

3. *state conversion conditions* that determine the possibility of inter-conversion between states via the usage of free operations and free states. These conditions, either necessary or sufficient (sometimes both), are sometimes phrased as *monotones*, i.e. the transition is possible if a particular function decreases in the transition $\rho \to \rho'$.

A classic example of resource theory comes from identifying entangled states as a resource. Suppose that Alice and Bob are two distant parties that are capable of creating any local quantum states in their own labs. Furthermore, since classical communication is well established today, they may easily communicate with each other classically (meaning they can send each other classical bits of information such as "001101..."). Such additional information might allow them to create classical correlations between their quantum states. This set of operations are known as Local Operations and Classical Communication (LOCC) [41, 48], which defines a set of free operations and states. However, if Alice and Bob are allowed only such operations, it is then impossible for them to create entanglement. Therefore, any prior entangled state that they share becomes a valuable resource, that they would aim to manage well. In Ref. [41], it was shown that if Alice and Bob have n copies of a certain partially entangled state $\rho_{\mathrm{AB}}^{\otimes n}$, they might be able to, via LOCC operations, concentrate the amount of entanglement by producing m copies of the maximally entangled state (where m is smaller than n). Such an task is called entanglement distillation, and since its theoretical introduction in [41], much experimental progress has also been done, in order to distil entanglement for the use of long-distance quantum communication [71–73].

In the recent years, quantum resource theories have been studied not only in its generality, for any restricted operations placed on quantum systems [75, 76], but also in particular those related to entanglement theory [41, 77, 78], coherent operations [42, 43], or energetically in thermodynamics [79, 80]. Table 3.1 provides a summary and comparison of the main characteristics for several resource theories. Though entanglement theory is the most extensively studied case out of these resource theories, due to the great similarity in mathematical framework, results can often be extended to the other quantum resource theories as well [81–83].

[1] Any state which is not a free state is then called a resource state.

Resource theory	Free operations	Free states	State conversion conditions
Entanglement (LOCC operations [48])	Local unitaries and classical communication	Any separable state $\rho_{AB} = \sum_i p_i \rho_{A,i} \otimes \rho_{B,i}$	$\|\psi\rangle\langle\psi\|_{AB} \to \|\phi\rangle\langle\phi\|_{AB}$ iff $S(\psi_A) \geq S(\phi_A)$.
Asymmetry w.r.t. a group G [74]	Any CPTPM $\mathscr{E}$ such that for any unitary representation U_G, $g \in G$, $\mathscr{E}\left[U_g(\cdot)U_g^\dagger\right] = U_g \mathscr{E}(\cdot) U_g^\dagger$.	Any state ρ such that $\forall U_g$, $U_g \rho U_g^\dagger = \rho$	For the symmetric group given by $\mathrm{Sym}_G(\rho) = \left\{g \in G : U_g \rho U_g^\dagger = \rho\right\}$, then $\rho \to \rho'$ only if $\mathrm{Sym}_G(\rho) \subseteq \mathrm{Sym}_G(\rho')$.
Coherence w.r.t. a basis $\{\|i\rangle\}$ [43]	Incoherent operations, i.e. any CPTPM $\mathscr{E}$ such that for any $\rho \in \mathscr{I}$, where $\mathscr{I}$ is the set of states diagonal w.r.t. basis $\{\|i\rangle\}$, $\mathscr{E}(\rho) \in \mathscr{I}$.	Any $\rho \in \mathscr{I}$ diagonal in the basis $\{\|i\rangle\}$	For the relative entropy of coherence given by $\mathbf{C}_{RE}(\rho) = \min_{\sigma \in \mathscr{I}} D(\rho \| \sigma)$, $\rho \to \rho'$ only if $\mathbf{C}_{RE}(\rho) \geq \mathbf{C}_{RE}(\rho')$.
Purity (Section 3.2.1)	Unitary operations	Maximally mixed states	Majorization: $\rho \to \rho'$ iff $\mathrm{eig}(\rho) \succ \mathrm{eig}(\rho')$ (Eq. (2.4.1)).
Thermodynamics (Section 3.2.2)	Energy-preserving unitary operations	Gibbs states of the form in Eq. (3.2.8)	Thermo-majorization (see Section 3.2.2)

Table 3.1: A comparison between several examples of resource theories.

Returning back to the paradigm of entanglement theory: if one considers the set of LOCC operations as free operations, and separable states as free states, then any state that contains entanglement is a resource. The resource theoretic framework has been adapted in the approach towards quantum thermodynamics, as we shall see in the next few sections.

3.2. THERMODYNAMIC RESOURCE THEORIES (TRTS)

3.2.1. NOISY OPERATIONS (NO)

The framework of *noisy operations*, which is perhaps the simplest known resource theory, is characterized by the following:

1) free resources are maximally mixed states of arbitrary dimension,

2) all unitary transformations and the partial trace are allowed operations.

Since noisy operations are not concerned with energetic constraints, and focus only on the information (or disorder) contained in systems, it has also been referred to as the *resource theory of informational nonequilibrium*, or the *resource theory of purity*. This toy model for thermodynamics was first described in [79] and has its roots in the problem of exorcising Maxwell demon [27, 84], building on the resource theory of entanglement manipulations [41, 85–88]. The reader is referred to [89] for an extensive, detailed review of this framework.

It was shown in [79] that when considering state transitions $\rho_S \to \rho'_S$, where $\rho_S, \rho'_S \in$

$S(\mathscr{H}_S)$, then the class of noisy operations is equivalent to the set of mixtures of unitaries acting on system S. To see this, note that a quantum channel $\mathscr{E}_{\text{Noisy}}$ is a noisy operation if and only if there exists an ancilla system R (with dimension d_R) such that

$$\rho'_S = \mathscr{E}_{\text{Noisy}}(\rho_S) = \text{tr}\left[U_{SR}\left(\rho_S \otimes \frac{\mathbb{1}_R}{d_R}\right)U_{SR}^\dagger\right]. \tag{3.2.1}$$

Since arbitrary unitaries can be performed for free, in particular we may consider only the case where ρ_S, ρ'_S are diagonal in the same basis[2], and therefore we need only to consider $\mathscr{E}_{\text{Noisy}}$ as the representation of a classical channel. Note that also since only unitaries are allowed, $\mathscr{E}_{\text{Noisy}}$ by definition preserves the maximally mixed state $\rho_S = \frac{\mathbb{1}_S}{d_S}$, i.e. it is a unital channel. Therefore, $\mathscr{E}_{\text{Noisy}}$ may be represented by a bistochastic matrix. By the Birkhoff-von Neumann theorem, any bistochastic matrix may be written in terms of a mixture of permutation matrix (which are unitary operations). The converse is true: any mixture of permutation matrices is bistochastic.

Earlier in Section 2.4, we have seen the relation between bistochastic matrices and majorization. Therefore the condition that ρ_S can be transformed into ρ'_S via noisy operations, is equivalent to $\text{eig}(\rho_S)$ majorizing $\text{eig}(\rho'_S)$:

$$\rho_S \xrightarrow[\text{NO}]{} \rho'_S \qquad \Longleftrightarrow \qquad \text{eig}(\rho_S) \succ \text{eig}(\rho'_S). \tag{3.2.2}$$

3.2.2. THERMAL OPERATIONS (TO)

How are noisy operations related to thermodynamical interactions? Note that the maximally mixed state (which we allow as free states in noisy operations) has a few unique properties: firstly, it is the state with the maximum amount of von Neumann entropy. It is also the state which is preserved by any noisy operation. According to the maximum entropy principle that we have explained in Chapter 1, a state which has equilibrated will take on the form of maximum entropy, under the constraint of conserved quantities (in particular, total energy). In particular, if the Hamiltonian of the system is fully degenerate, i.e. all microstates have the same amount of energy, then the Gibbs state is then the maximally mixed state, which has maximum entropy. On the other hand, given some arbitrary Hamiltonian, under the constraint that average energy is fixed, then the state with maximum entropy is given by the Gibbs thermal state of the form in Def. 2.9. Since the Gibbs state commutes with the Hamiltonian, it is also stationary under the evolution of the Hamiltonian.

In Chapter 1, we have seen that much work has been done to derive the emergence of Gibbs states in equilibration processes from the basic principles of quantum theory. From this, we have concluded that most quantum systems (i.e. generic Hamiltonians and initial states) will eventually equilibrate and tend towards the Gibbs state. This motivates the usage of Gibbs states as free states in the resource theory framework for thermodynamics.

With these in mind, thermal operations were first considered in [90] and further developed in [80, 91] in order to model the interaction of quantum systems with their larger immediate steady-state environment. The first restriction considered is that of *energy-conserving unitary dynamics*: since systems are described by quantum states, the evolution should be described by unitary evolutions U_{SR} across the closed system (S) and bath

[2] Otherwise, one may simply define a similar noisy operation which first transforms ρ to the basis of ρ', before applying $\mathscr{E}_{\text{Noisy}}$.

(R). Furthermore, the thermodynamical process described should preserve energy over the global system. Note that the demand that energy is conserved, implies that U_{SR} commutes with the total Hamiltonian[3].

In Chapter 4, we will show that if the considered free operations are only those of unitaries that commute with the Hamiltonian, then the thermal state as defined in Eq. (3.2.8) has a unique physical significance: they are the only states which cannot be used to extract work. This further justifies the usage of Gibbs states as free states.

Therefore, let us now see the definition of thermal operations. Consider a system S which is governed by Hamiltonian $\hat{H}_S$. For any real positive value $\beta \in \mathbb{R}^+$, a quantum channel $\mathscr{E}_{\text{TO}}$ is a β-thermal operation if and only if there exists:

1. (free states) a Hamiltonian $\hat{H}_R$, with a corresponding Gibbs state

$$\tau_R^\beta = \frac{1}{Z} e^{-\beta \hat{H}_R}, Z = \text{tr}\left(e^{-\beta \hat{H}_R}\right), \tag{3.2.3}$$

2. (free operations) and a unitary U such that $[U, \hat{H}_{SR}] = 0$, such that

$$\mathscr{E}_{\text{TO}}(\rho_S) = \text{tr}\left[U_{SR}\left(\rho_S \otimes \tau_R^\beta\right) U_{SR}^\dagger\right]. \tag{3.2.4}$$

In the special case where $\hat{H}_S = \mathbb{1}_S$ and $\hat{H}_R = \mathbb{1}_R$, thermal operations $\mathscr{E}_{\text{TO}}$ reduce to noisy quantum operations.

Now, consider a system described by $\hat{H}_S$, and quantum states ρ_S, ρ_S'. What are then, the state transition conditions for $\rho_S \xrightarrow[\text{TO}]{} \rho_S'$? Ref. [80] first considered the question of asymptotic conversion rates, i.e. the optimal rate of conversion $R(\rho_S \to \rho_S') = \frac{m}{n}$ such that $\rho_S^{\otimes n} \to \rho_S'^{\otimes m}$, for the limit $n \to \infty$. Later, Ref. [91] derived a set of majorization-like conditions which determine state transition conditions for a single copy of ρ_S and ρ_S' which are block-diagonal (with respect to $\hat{H}_S$).

3. (State conversion conditions) Conditions for state transitions to occur via thermal operations are called *thermo-majorization*. To define these conditions, first let us explain what is a thermo-majorization curve.

Definition 3.1 (Thermo-majorization curve)**.** *For any state-Hamiltonian pair $(\rho_S, \hat{H}_S)$ where ρ_S is block-diagonal w.r.t. $\hat{H}_S$, this means that $\rho_S, \hat{H}_S$ share a common basis which we denote as $\{|E, g_E\rangle\}_{E,g_E}$, where E runs across the distinct energy eigenvalues, and g_E runs across degeneracies corresponding to the eigenvalue E. Let ρ_S be a state such that* $\text{rank}(\rho) = d$*, and*

$$\rho_S = \sum_{E,g_E} p_{E,g_E} |E, g_E\rangle\langle E, g_E|_S, \tag{3.2.5}$$

so that p_{E,g_E} are the eigenvalues of ρ_S corresponding to energy eigenvalue E. The β thermo-majorization curve $T_\beta(\rho_S, \hat{H}_S)$ is defined by first ordering the eigenvalues to have $p^{\downarrow\beta} = (p_1, \cdots, p_d)$ with the corresponding energy eigenvalues $E_1, \cdots, E_d$ such that

$$p_1 e^{\beta E_1} \geq p_2 e^{\beta E_2} \geq \cdots p_d e^{\beta E_d}. \tag{3.2.6}$$

[3]The joint Hamiltonian is assumed to be the sum of individual free Hamiltonians, i.e. $\hat{H}_{SR} = \hat{H}_S \otimes \mathbb{1}_R + \mathbb{1}_S \otimes \hat{H}_R$.

Such an ordering is called β-ordering. The thermo-majorization curve of $(\rho_S, \hat{H}_S)$ is a concave, piecewise linear curve, defined by joining all the points

$$\left\{(0,0),\ \left(e^{-\beta E_1}, p_1\right),\ \left(e^{-\beta E_1}+e^{-\beta E_2}, p_1+p_2\right),\ \cdots,\ \left(\sum_{i=1}^{d} e^{-\beta E_i}, \sum_{i=1}^{d} p_i\right)\right\}. \tag{3.2.7}$$

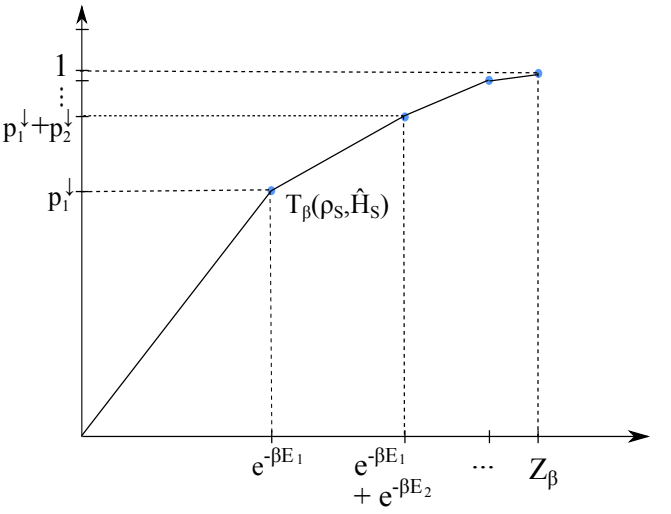

Figure 3.1: An example of a thermo-majorization curve of a state-Hamiltonian pair $T_\beta(\rho_S, \hat{H}_S)$.

Fig. 3.1 shows an example of a thermo-majorization diagram defined by the points in Eq. (3.2.7). It is proven in [91] that the comparison of two curves dictate the possibility of state transition from one state to another via thermal operations.

Theorem 3.1. *Given state-Hamiltonian pairs $(\rho_S, \hat{H}_S)$ and $(\rho'_S, \hat{H}'_S)$, the state transition $\rho_S \xrightarrow[TO]{} \rho'_S$ can happen if and only if $T_\beta(\rho_S, \hat{H}_S) \geq T_\beta(\rho'_S, \hat{H}'_S)$, i.e. the β thermo-majorization curve of $(\rho_S, \hat{H}_S)$ lies above that of $(\rho'_S, \hat{H}'_S)$. In this case, we say that ρ_S thermo-majorizes ρ'_S.*

Note that if we consider the state $\tau_S^\beta = \frac{1}{\mathrm{tr}\left(e^{-\beta \hat{H}_S}\right)} e^{-\beta \hat{H}_S}$, then the thermo-majorization curve $T_\beta(\tau_S^\beta, \hat{H}_S)$ simply forms a straight line with endpoints $(0,0)$ and $(Z_\beta, 1)$. Therefore, for any other block-diagonal state ρ_S, Theorem 3.1 implies that $\rho_S \xrightarrow[\mathrm{TO}]{} \tau_S^\beta$ is always possible via a β-thermal operation.

3.2.3. CATALYTIC THERMAL OPERATIONS (CTOS)

Catalytic thermal operations are extensions of thermal operations, where in addition to the same free resources and operations, catalysts that remain unchanged are allowed. In other

words, $\rho_S \xrightarrow[\text{CTO}]{} \rho_S'$ is possible via a β-catalytic thermal operation iff there exists

1. (free states) a Hamiltonian $\hat{H}_R$, with a corresponding Gibbs state

$$\tau_R^\beta = \frac{1}{Z} e^{-\beta \hat{H}_R}, Z = \mathrm{tr}\left(e^{-\beta \hat{H}_R}\right), \tag{3.2.8}$$

2. (catalysts) any additional finite-dimensional quantum state ω_C with Hamiltonian $\hat{H}_C$,

3. (free operations) and a unitary U_{SRC} such that $[U_{SRC}, \hat{H}_{SRC}] = 0$, such that

$$\mathrm{tr}_R\left[U_{SRC}\left(\rho_S \otimes \tau_R^\beta \otimes \omega_C\right) U_{SRC}^\dagger\right] = \rho_S' \otimes \omega_C. \tag{3.2.9}$$

Since the catalyst ω_C is returned exactly, such a process is also referred to as *exact catalysis*.

CTOs are a non-trivial generalization of TOs, since there exists transitions that cannot occur via TOs, but are made possible by the presence of a catalyst. The analysis of these operations are one of the main scientific contributions of this thesis, and will be studied in extensive detail in Chapters 4 and 5. In particular, in Chapter 4 we establish:

4. (state transition conditions) For $\rho_S \xrightarrow[\text{CTO}]{} \rho_S'$ to occur, whenever ρ_S, ρ_S' are block-diagonal, then the transition is possible via CTOs iff for all $\alpha \geq 0$,

$$F_\alpha(\rho_S, \hat{H}) := \beta^{-1}\left[\ln Z + D_\alpha(\rho_S \| \tau_S^\beta)\right] \tag{3.2.10}$$

is non-increasing, i.e. $F_\alpha(\rho_S, \hat{H}) \geq F_\alpha(\rho_S', \hat{H})$[4].

In Chapter 5, we consider *inexact catalysis*, which corresponds to the case where ω_C is not returned exactly, but a small *catalytic error* is allowed. There, we show that depending on how the catalytic error is quantified, different subsets of the second laws as expressed in Eq. (3.2.10) hold.

3.2.4. GIBBS PRESERVING MAPS (GPS)

The most generic type of model for thermodynamical resource theories is called *Gibbs preserving maps*. To be understood literally, this means that the set of free operations is simply the set of all CPTPMs that preserve the Gibbs state of inverse temperature β, i.e.

$$\mathscr{E}_{GP}\left(\tau_S^\beta\right) = \tau_S^\beta. \tag{3.2.11}$$

One can view GPs as highlighting the "bottomline" of any model for thermodynamical interactions: it allows any map that preserves the Gibbs thermal state. It differs non-trivially from the set of catalytic thermal operations: although any thermal operation corresponds to a Gibbs preserving map, however in general Gibbs preserving maps may act on block-diagonal initial states to create final states that are non block-diagonal. This cannot occur under via thermal operations. GPs, however, are the least studied amongst all thermodynamical models since there is no explicit physical process that describes the full set of GPs.

[4] This is proven in Theorem 4.5, and is also Proposition 1 of this thesis

3.3. DEVELOPMENTS ON RESOURCE THEORIES

The simplicity of a resource theoretic approach towards quantum thermodynamics is its main appeal and power, although it may at the same time be its weakness. Given the large amount of past approaches in modelling thermodynamical interactions, such as Master/Linblad equations governing open quantum systems [19, 20, 44, 92–94] (especially those involving strong coupling Hamiltonians between systems and bath [95–97]), time dependence in Hamiltonians (for example quenches [98, 99]) etc, the question arises as to how TRTs relate to these different approaches. Therefore, since its most primitive version of noisy/thermal operations, various works have endeavoured to extend and connect the usage of TRTs with other approaches. In particular, we list some important results to date:

1. *Inclusion of catalysts* (contributed in Chapter 4 and 5 of this thesis)
   Catalysts are additional quantum systems that can be used in a thermal operation, but have to be returned to their exact initial state. With this extension, any experimental apparatus used to implement TOs can be modelled as additional quantum systems, and be included into the framework of thermal operations. The criteria and guidelines for choosing appropriate catalyst states have been one of the main focuses of this thesis. On the other hand, different usages of catalyst such as correlated catalysts [100], and catalysts which have coherence in the energy eigenbasis [101] have been investigated to date.

2. *Autonomous thermal operations via clock models*
   A fully autonomous model of thermodynamical interactions would simply be described by a time independent Hamiltonian. Such a scenario usually depicts a naturally arising physical process, since the systems simply evolve spontaneously according to a fixed Hamiltonian without any control from an observer. In contrast, the resource theoretic framework allows the implementation of arbitrary unitaries, assuming that an external experimenter has control over the system. However, it has been made precise in [102, 103] that by considering explicit quantum clocks, and a time-independent Hamiltonian on the global system, one may effectively implement unitaries on the system. Such a global Hamiltonian usually performs an operation on the system, controlled on the clock's state.

3. *Relation to Gibbs preserving maps*
   In [104], it is shown that TOs are a strict subset of Gibbs preserving maps, i.e. the set of all quantum channels which preserve the Gibbs thermal state. However, if one considers only the set of all quantum states block-diagonal in the energy eigenbasis, then any Gibbs preserving map can be written as a TO. Therefore, for investigations involving only block-diagonal quantum states, the paradigm of TOs is fully general.

4. *Equivalence to other operations*
   In order to study the fundamental limits to thermodynamics, TOs consider a large set of operations: the experimenter is allowed to use an arbitrary thermal bath, and any energy-preserving unitary. This allows for the derivation of statements holding for full generality, however, one may question if there exists simple operations that would also achieve the full power of TOs. Recently it has been shown that such any thermal operation corresponds to a *coarse operation* [105], where the latter involves qubit baths, level

transformations (LTs, namely the lifting/lowering energy levels of the Hamiltonian) and thermalization. This partially reconciles the TRT framework with various approaches in quantum thermodynamics [28, 106–109]. Also, for NOs, it has been shown that the size of the heat bath (i.e. the maximally mixed state used) needs only to be at most equal to the size of the system [110]. These simplifications pave the way to designing protocols that achieve the optimal state transitions as predicted by the TRT frameworks.

5. *Relation with fluctuation theorems*
   A distinct approach to quantum thermodynamics, commonly known as fluctuation relations (FR) has been independently progressing in parallel to the development of TRTs [11, 111–113]. A handful of experimental verifications for these relations have been demonstrated, both in the classical [114] and quantum regime [115, 116]. However, the stark conceptual differences between FRs and TRTs have prevented them, so far, to be connected. Recently, the possibility of connecting both to form a harmonious picture of thermodynamics has been explored [117, 118]. Should this be achieved, it would provide us potential means to experimentally verify TRTs by making use of FR demonstrations.

6. *Inclusion of other conserved quantities*
   A quantum system may in general obey several conservation laws other than total energy, where the conserved quantities are represented by operators on the system which do not generally commute. In such cases, it was not clear whether such systems thermalize and what would free states look like. In [119, 120], such scenarios have been studied in order to model not only energetic/information exchanges in thermodynamics, but also including exchanges of other non-commuting observables.

3.4. WORK EXTRACTION

We have seen that thermodynamic resource theories provide us a framework that allows for the derivation of conditions for a system to evolve from one state to another, while explicitly considering processes that conserve energy. However, as we have also seen in Chapter 1, a central concept in thermodynamics is the consumption/extraction of work, which is the output/input of ordered energy to a system. Therefore, we must ask the question: in the context of resource theories, what does it mean to extract work?

To gain some intuition for a rigorous formulation, let us first consider the classical picture of thermodynamics. There, work is often pictured as the effect of storing potential energy on some specific system, for example designing a protocol involving a hanging weight, such that in the end the weight is lifted by some height Δx. How could one achieve such a task then, given only immediate resources which are thermal? In classical thermodynamics, it is a long-standing qualitative observation that one cannot extract work from a thermal reservoir (this has been formulated in the Kelvin statement, given on page 3); however given two reservoirs at different temperatures, one can then design protocols that extract work. A common approach (found in any standard thermodynamics textbook such as [2–5]) is to consider a heat engine, where a machine system interacts with two different heat baths successively, and undergoes a cyclic process. An example of such a "machine" could be a cylinder of ideal gas, where the volume is changeable via a piston. By allowing the gas to go through a series of isothermal/adabatic expansions/contractions while interacting with two reservoirs at different temperatures, one may analyze the net energy/heat flow

in and out of this machine system. By energy conservation methods, one can then calculate an estimate of the energy output on the weight attached to such a piston, while assuming that energy lost/dissipated (for example, via friction) is negligible.

WORK IN THE QUANTUM NANOREGIME

With such a classical picture in mind, the question of interest is then as follows: given a quantum state-Hamiltonian pair $(\rho_S, \hat{H}_S)$, how should one quantify the amount of work extractable from such a state?

Prior to the introduction of resource theoretic frameworks, earlier approaches [28, 106–109] in quantum thermodynamics have considered different sets of operations such as LTs and thermalization. These operations are non-energy preserving in general, for example LT involves the changing of energy levels in the Hamiltonian. Therefore, for each operation, one may attach an amount of "work" done to/by the system [121]. In particular, much discussion has gone into how one should differentiate work from heat [108, 122–124] in the quantum regime. Although both contribute to a change in energy of the system, work stored is of an *ordered* form, and therefore can be extracted and used, while heat is irreversibly dissipated/lost and cannot be converted into useful energy. Though a seemingly simple problem, there is no concensus among the community as to how work should be defined.

Another approach which is commonly used in the resource theoretic framework [91, 125] (although not restricted to resource theories), is to explicitly consider an ancillary system called the *battery* (denoted as W), and consider the possibility of the state transition

$$\rho_S \otimes \rho_W \xrightarrow[\text{TO}]{} \rho'_S \otimes \rho'_W, \tag{3.4.1}$$

for any arbitrary final state ρ'_S, and some specific battery states ρ_W, ρ'_W. Commonly used models of battery Hamiltonians include a two-level qubit that has a tunable energy gap (wit) [91, 125], a harmonic osciilator [126], or a system with quasi-continuous energy levels (as used in Chapter 6). For an explicit example, if we use the two-level qubit battery such that $\hat{H}_W = W_{\text{ext}}|1\rangle\langle 1|_W$, then a transition from the state $\rho_W = |0\rangle\langle 0|_W$ to $\rho'_W = |1\rangle\langle 1|_W$ correspond to extracting an amount of work equal to W_{ext}.

Most often, the explicit battery model (i.e. its Hamiltonian $\hat{H}_W$) does not affect the amount of work stored/used. However, it does depend on the initial and final battery states ρ_W, ρ'_W. The central question of defining work still remains: how should one then quantify the amount of work stored in the battery, as a function of these initial and final states?

AVERAGE WORK

In [126–129], explicit protocols (defined by successive steps like LTs, thermalization, or unitary operations) were analyzed and the amount of average energy change in the battery can be quantified by

$$\Delta W = \mathrm{tr}(\hat{H}_W \rho'_W) - \mathrm{tr}(\hat{H}_W \rho_W). \tag{3.4.2}$$

Since the amount of work extracted depends on the average energy change of the battery, which is subjected to random processes (such as thermalization), work is therefore treated as a random variable. Some of these works have shown that for example, an optimal amount of average work (equal to the free energy of the system) can be drawn [126, 128], or that Carnot efficiency can be achieved [126]. In such cases, the amount of entropy has to be

separately analyzed, in order to show that heat contributions to the average energy increase are either negligible, or accounted for in some way. This is because in [108], it is shown that such protocols could produce work with fluctuations of the same order.

SINGLE-SHOT AND DETERMINISTIC WORK

In order to address the problem of large fluctuations in the random variable of work, concepts in single-shot information theory have been brought into the realm of quantum thermodynamics, in order to more accurately describe how one should distinguish work from heat. However, even when restricted to single-shot work extraction, different definitions have been used, such as:

1. drawing at least an amount of work W_{ext} except with probability ε [45],

2. $(\varepsilon, \delta)-$deterministic work: finding the probability distribution of work variable in some interval $\left[W_{\text{ext}} - \delta, W_{\text{ext}} + \delta\right]$ except with some probability ε [106, 108], or

3. fixing the initial battery state as some energy eigenstate $|E_j\rangle\langle E_j|_W$, while allowing the final battery state $\rho_W^1 \approx_\varepsilon |E_j + W_{\text{ext}}\rangle\langle E_j + W_{\text{ext}}|_W)$. This is a definition which is common to resource theoretic approaches to quantifying work [91, 125, 130].

Before ending the discussion on defining work, it is worth noting that besides work extraction, another frequently investigated thermodynamic protocol is cooling [20, 131, 132]. This is analogous to having both heat engines and refridgerators in classical thermodynamics. For such protocols, the definition of cooling is much less debated, since the aim of cooling is not to produce final battery states which can later be used, but simply to lower the amount of average energy in a targeted system.

4

THE SECOND LAWS FOR QUANTUM THERMODYNAMICS

The Clausius formulation of the classical macroscopic second law tells us which state transformations are so statistically unlikely that they are effectively forbidden. This applies to systems composed of many particles interacting. However, we are seeing that one can comprehend thermodynamics even when only a small number of particles are interacting with a heat bath. Is there a second law of thermodynamics in this regime? Here, we find that for processes which are cyclic, the second law for microscopic systems takes on a different form compared to the macroscopic scale, imposing not just one constraint on state transformations, but an entire family of constraints. In particular, we find a family of free energies which generalize the traditional one, and show that they can never increase. The ordinary second law relates only to one of these free energies, with the remainder imposing additional constraints on thermodynamic transitions. These second laws are relevant for small systems, and also apply to individual macroscopic systems interacting via long-range interactions, which only satisfy the ordinary second law on average. By making precise the definition of thermal operations, the laws of thermodynamics are unified in this framework, with the first law defining the class of operations, the zeroeth law emerging as an equivalence relation between thermal states, and the remaining laws being a monotonicity property of our generalized free energies.

4.1. INTRODUCTION

The original formulation of the second law, due to Clausius [7], states that "Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time". In attempting to apply Clausius's statement of the second law to the microscopic or quantum scale, we immediately run into a problem, because it refers to cyclic processes in which there is *no other change* occurring at the same time, and at this scale, it is impossible to design a process in which there is no change, however slight in our devices and heat engines. Interpreted strictly, the Clausius statement of the second law, applies to situations which never occur in nature. The same holds true for other versions of the second law, such as the Kelvin-Planck statement, where one also talks about cyclic processes, in which all other objects beside the system of interest are returned back to their original state.

Here, we derive a quantum version of the Clausius statement, by looking at processes where a microscopic or quantum system undergoes a transition from one state to another, while the environment, and working body or heat engine is returned back to their original state. While macroscopically, only a single second law restricts transitions, we find that there are an entire family of more fundamental restrictions at the quantum level. At the macroscopic scale, and for systems with short range correlations, this entire family of second laws become equal to the ordinary second law, but outside of this regime, these other second laws impose additional restrictions on thermodynamical transitions. What's more, one needs to specify " how cyclic" the process is, in order to determine which subset of these second laws hold. We also derive in this work, a zeroeth law of thermodynamics, which is stronger than the ordinary zeroeth law.

For thermodynamics at the macroscopic scale, a system in state ρ can be transformed into state ρ' provided that the free energy goes down, where the free energy for a state ρ is

$$F(\rho) = \langle E(\rho) \rangle - kTS(\rho), \tag{4.1.1}$$

with T the temperature of the ambient heat bath that surrounds the system, k, the Boltzmann constant, $S(\rho)$ the entropy of the system, and $\langle E \rangle$ its average energy. This is a version of the second law, where we also use the fact that the total energy of the system and heat bath must be conserved. This criterion governing state transitions is valid if the system is composed of many particles, and there are no long range correlations. In the case of microscopic, quantum or highly correlated systems, a criterion for state transitions of a total system was proven in [91] and named thermo-majorization (See Figure 4.2). This criterion serves as a second law in some cases (see also the reformulation of [106]). However, here, we will see that if elevated to such high status without sufficient care, it can be violated. Namely, we will give examples where $\rho \to \rho'$ would violate the thermo-majorization criterion, but nonetheless, the transition is possible via a cyclic process in which a working body σ - an ancilla or catalyst - is returned back into its original state. The criteria of [91] is thus only relevant for systems without the involvement of such ancillatory systems.

This phenomenon is related to entanglement catalysis [133], where it can be shown that some forbidden transitions are possible, if we can use an additional system σ as a catalyst, i.e. we may have $\rho \not\to \rho'$ and yet $\rho \otimes \sigma \to \rho' \otimes \sigma$. In the case of thermodynamics, the catalyst σ may be thought of as a working body or heat engine which undergoes a cyclic process and is returned back into its original state. In deciding whether one can transform ρ into

ρ', one therefore needs to ask whether there exists a working body or other ancillas σ for which $\rho \otimes \sigma \to \rho' \otimes \sigma$ (see Figure 4.1). Thus, thermo-majorization should only be applied to total resources including all possible catalysts and working bodies and not the system of interest itself. In the case of entanglement theory, and when the catalyst is returned in exactly the same state, the criteria for when one pure state may be transformed into another has been found [134, 135] and they are called trumping conditions. We will generalise and adapt the trumping conditions to enable their application to the case of thermodynamics.

4.1.1. RESULTS AND CONTRIBUTIONS

Motivated by the statements of Kelvin and Clausius presented in Chapter 1, we generalize the framework of thermal operations detailed in Section 3.2.2 to consider *catalysts*, which are ancillary systems that undergo a cyclic process, i.e. they interact with other systems in a way such that at the end of the thermodynamic process, they are returned to their initial states. This allows for the crucial component of having an *inanimate material agency* that *undergoes no other change*, that facilitates a process without providing net energetic contributions. Examples of such systems include the machine component of a heat engine, which interacts succesively with different heat baths, undergoing a series of thermal expansion and adiabatic processes, finally outputs some amount of work before returning to its original state.

- We derive necessary conditions for state transitions when the involvement of any such cyclic component is allowed. These conditions can be phrased in terms of entropic quantities, which we coin as *generalized second laws*. They form additional restrictions to the set of possible transitions, when compared to the macroscopic second law. Moreover, we show that when investigating states which are block-diagonal in the energy eigenbasis, such conditions become necessary and sufficient. Our derivation of the second laws is information theoretic in nature, requiring none of the assumptions usually required for the second law to hold. This includes ergodicity, mixing, coarse-graining of degrees of freedom and lack of control over the system [1, 136].

4.1.2. CHAPTER OUTLINE

We begin in Section 4.2, by defining the notion of *catalytic thermal operations* (CTOs). The first law finds its place here as a statement regarding conservation of energy. In Section 4.3, we rigorously prove the importance of allowing only Gibbs states of a fixed temperature as free states. This allows us to identify the uniqueness of Gibbs states as free resources, and by defining an equivalence relation between different Gibbs states, we see that the temperature emerges as a unique parameter. This is an analog of the zeroeth law of thermodynamics.

We first consider fully degenerate Hamiltonians in Section 4.4 and derive the necessary and sufficient conditions for state transitions via CTOs. We show that these conditions can be phrased solely in terms of Rényi divergences. This is then generalized to the case of arbitrary, discrete Hamiltonians in Section 4.5, leading to a set of generalized second laws for block-diagonal states, which we summarize in Theorem 4.5.

Finally, Section 4.6 addresses the case of arbitrary quantum states (instead of only the block-diagonal ones). By invoking data processing inequality, we show that the generalized

second laws stated in Section 4.5 are also necessary conditions for arbitrary quantum states. We end with some concluding remarks in Section 4.7.

4.2. CATALYTIC THERMAL OPERATIONS

Despite the mathematical simplicity of thermal operations as a resource theory towards quantum thermodynamics, refinements to the framework are much warranted. One of the main critiques of the theory is that though rooted in the very basics of quantum theory, it does not sufficiently consider how thermodynamical interactions occur in reality. For example, how does one perform an energy-preserving unitary? This is done in practice by turning on/off an interaction Hamiltonian for some time Δt. A way to incorporate such a time-dependent Hamiltonian, is to therefore consider the addition of an *ancillary* quantum state C, where the interaction can be turned on/off depending on the state of C. Such an ancilla acts like a "clock", to govern the interaction time in order to implement unitary operation. Therefore, in principle one should also consider the possibility of additional quantum states participating in the process, as part of the experimental apparatus.

Furthermore, consider the picture of heat engine cycles, which has been at the very core of classical thermodynamics since the field was established in the 1800s. Indeed, the performance of a heat engine is often analyzed by how a machine interacts between multiple thermal baths, undergoing a cyclic process while extracting work. Therefore, in essence, a machine plays the role of an agent which does not function as an energy source/sink, but facilitates the transfer of energy in a process such as work extraction. Such a component should therefore be explicitly accounted for, in any framework that attempts to model thermodynamical interactions.

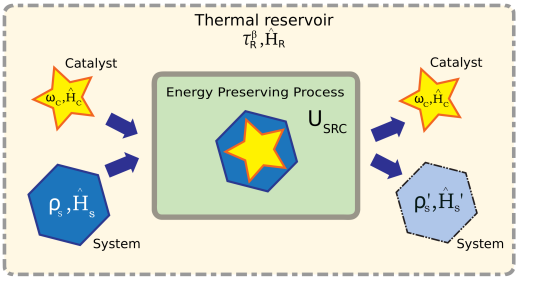

Figure 4.1: When can a state ρ_S with Hamiltonian $\hat{H}_S$ be transformed to a state ρ_S' and Hamiltonian $\hat{H}_S'$? In order to do so via catalytic thermal operations, one can couple the system to a heat bath $\tau_R^\beta = e^{-\beta \hat{H}_R}/Z_R$ with Hamiltonian $\hat{H}_R$, use any additional devices in the process as long as they are returned back in their original state (thus we may think of them as a catalyst - ω_C), and perform any quantum-mechanical action as long as we preserve the overall energy.

This motivates the formulation of *catalytic thermal operations*, which allow for the usage of such ancilla states, as long as they are returned at the end of the process in their initial states, so that we are prevented from using them as a resource state (see Figure 4.1). More concretely, given an initial quantum state ρ_S governed by some Hamiltonian $\hat{H}_S$, a β-catalytic thermal operation is defined by three components:

1. a thermal bath decribed by any Hamiltonian $\hat{H}_R$, with its corresponding Gibbs state τ_R^β at inverse temperature β, as seen in Eq. (3.2.8),
2. any catalyst ω_C with its Hamiltonian $\hat{H}_C$,
3. a unitary U_{SRC} such that $[U_{SRC}, \hat{H}_S + \hat{H}_R + \hat{H}_C] = 0$,

such that

$$\mathrm{tr}_R \left[U_{SRC} \left(\rho_S \otimes \tau_R^\beta \otimes \omega_C \right) U_{SRC}^\dagger \right] = \rho_S' \otimes \omega_C. \tag{4.2.1}$$

Recall the demand that the unitary commutes with the total Hamiltonian implies that energy is conserved. Conversely, if a process conserves energy for any arbitrary state. then it must commute with the Hamiltonian. The equivalence of this paradigm to others has already been addressed in [80]. The first law of thermodynamics is therefore viewed not as something derived as a consequence, but rather, a physical law that nature submits to in any thermodynamical interaction.

In Section 3.2.2, it has been shown that thermo-majorization is the criterion that determines the possibility of a state transition. However, the relaxation from thermal operations to catalytic thermal operations alter this criterion. We observe examples where $\rho_S \xrightarrow[\text{TO}]{} \rho_S'$ violates the thermo-majorization criterion, but nonetheless there exists a catalyst ω_C such that $\rho_S \otimes \omega_C \xrightarrow[\text{TO}]{} \rho_S' \otimes \omega_C$ is possible. Similar examples of such transitions can be found in the resource theory of entanglement [133]. In deciding whether one can transform ρ_S into ρ_S', one therefore needs to ask whether there exists a working body or other ancillas ω_C for which $\rho_S \otimes \omega_C \xrightarrow[\text{TO}]{} \rho_S' \otimes \omega_C$ (see Figure 4.1). Since ω_C is returned exactly, we call this *exact catalysis*, as opposed to *inexact catalysis* which we shall see later in Chapter 5. Thus, thermo-majorization should only be applied to total resources including all possible catalysts, not only the system of interest itself.

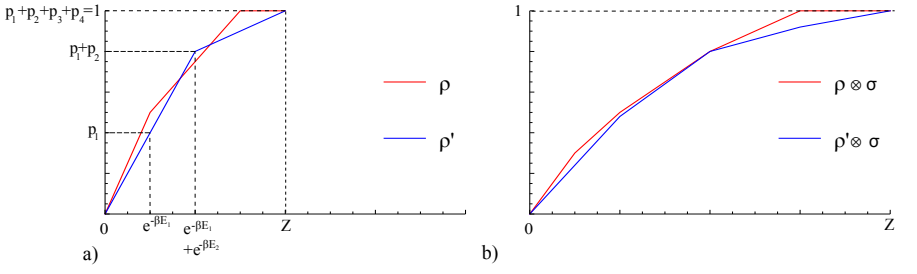

Figure 4.2: This figure shows an example of thermo-majorization diagrams for two states ρ, ρ'. Figure a) shows that because the diagrams cross each other, we cannot transform $\rho \xrightarrow[\text{TO}]{} \rho'$ without investingwork (or visa-versa). However, by using a catalyst ω which is returned in its initial state, we see in Figure (b) that $\rho \otimes \omega$ thermo-majorizes $\rho' \otimes \omega$. Therefore, the transition from $\rho \xrightarrow[\text{CTO}]{} \rho'$ is possible without additional work.

In the case of entanglement theory, and when the catalyst is returned in exactly the same state, the criteria for when one pure state may be transformed into another has been

found [134, 135] and they are called trumping conditions. We will generalize and adapt the trumping conditions to enable their application to the case of thermodynamics.

4.3. ZEROETH LAW OF QUANTUM THERMODYNAMICS

In this section, we first spell the proof for the zeroeth law in the framework of thermal operations. This implies constructing a notion of thermal equilibrium between different state-Hamiltonian pairs.

We accomplish this, firstly, by singling out Gibbs states as the unique set of free states allowed. More precisely, if we allow arbitrary energy preserving unitaries, then the only free states that do not give rise to trivial state conversion conditions is the set of Gibbs states (with their corresponding Hamiltonians) of a fixed inverse temperature. This is directly related to work extraction, since one should make sure that work cannot be extracted from a free state. Otherwise, one could, by using indefinite amounts of free states, extract enough work in order to facilitate any state transformation. Therefore, we want to show that given a system Hamiltonian $\hat{H}_A$, and the corresponding thermal state τ_A^β with some fixed inverse temperature β, then by allowing arbitrarily many copies of any state $\rho_A \neq \tau_A^\beta$, one can always extract work deterministically by using energy preserving unitaries.

Let us first begin by showing that this is true for block-diagonal states[1]. We invoke the result of Pusz and Woronowicz [137] who introduced the notion of *passive* states, i.e. the states whose energy cannot be decreased by an arbitrary cyclic Hamiltonian evolution. Pusz and Woronowicz proved for general quantum systems described by a C^* algebra that the only completely passive states are either so called KMS states or ground states. Lenard [138] has translated their results to the case of finite-dimensional systems. For such systems, they proved the following:

(Theorem 3, [138]) Consider a block-diagonal state ρ corresponding to a Hamiltonian $\hat{H}$, and let $\{p_i\}$ and $\{E_i\}$ be the eigenvalues of ρ and $\hat{H}$ respectively. Then ρ is passive, iff $[\rho, H] = 0$, and for any i, j, $E_i > E_j$ implies that $p_i \leq p_j$ [2].

They further introduced a notion of *completely passive* states:

Definition 4.1 (Completely passive states)**.** *A state ρ is completely passive iff for all $n \in \mathbb{Z}^+$, $\rho^{\otimes n}$ is also passive.*

In particular, [138] has shown that if ρ is completely passive, then it must be either the ground state or the Gibbs state. We can also simply consider the Gibbs state, by noting that the ground state is simply an example of a Gibbs state in the particular case where the temperature $T \to 0$ (or $\beta \to \infty$).

Now, consider any non-passive state ρ_{np}. From the above characterization, one sees that it is possible to extract, *on average*, a non-zero amount of work simply by performing a

[1] The case where coherences exist between energy eigenstates can be dealt with, as shown in [126], by first decohering multiple copies of the state in its energy subspace. This will always lead to an athermal but block-diagonal state, where we can then apply the results for block-diagonal states again.

[2] This is also denoted in [138] as a structurally stable state.

population inversion (a switch of energy levels) $|E_i\rangle\langle E_i| \leftrightarrow |E_j\rangle\langle E_j|$ for some particular pair of indices i, j (for details, see proof of Theorem 4.1). By invoking typicality arguments, we show that by using many identical copies of ρ_{np}, then for small values of δ, ε, an amount of work $\delta-$close to the average work can always be extracted, except with failure probability ε. To conclude Theorem 4.2, one uses the mentioned result, that any state which is not a Gibbs state or a ground state, becomes non-passive, once we take sufficiently many copies. Therefore, the only states that do not allow $(\delta, \varepsilon)-$deterministic work extraction (recall Section 3.4) when given multiple copies, are the set of Gibbs states.

Before beginning the proof, we state for completeness Lemma 4.1 which is the main tool we use to invoke typicality.

Lemma 4.1 (Hoeffding inequality, [139])**.** *Consider $x = \sum_{i=1}^{N} h_i$, where $h_1, \cdots, h_N$ are independent random variables such that for every $i, h_i \in [a_i, b_i]$. Denote $R_i = b_i - a_i$. Then for any $\alpha > 0$, the probability*

$$P\left[|x - E[x]| \geq \alpha N\right] \leq e^{-\frac{2\alpha^2 N^2}{\sum_i R_i^2}}. \tag{4.3.1}$$

By using Lemma 4.1, we are ready to prove the main theorems in this section.

Theorem 4.1. *Given any Hamiltonian $\hat{H}$, consider a non-passive, block-diagonal state ρ. Then for any probability $\varepsilon > 0$, there exists $m \in \mathbb{N}$ such that given m copies of ρ, it is possible to extract a positive amount of work, except with probability ε.*

Proof. There are two main steps in this proof: first we construct the unitary that performs work extraction from a single copy of ρ, while storing the work in a battery system B similar to that of [126]. Subsequently, we form the joint unitary over the m systems and the battery system, and use the Hoeffding inequality to bound the amount of extracted work, albeit with some small failure probability.

Consider a non-passive, block-diagonal ρ_{A_k} on system A_k, for each $1 \leq k \leq m$. Then by the definition of passivity, there exists some i, j where $E_i > E_j$, $p_i > p_j$ holds. To extract work, let us use a battery with the Hamiltonian of a harmonic osciilator system, $\hat{H}_B = \sum_{n=1}^{N} n\hbar\omega |n\rangle\langle n|$, where $\hbar\omega = E_i - E_j$. Define the lowering operator $\hat{a}_B = \sum_{l=2}^{N} |l-1\rangle\langle l|$ and the joint energy-preserving unitary over a particular system A_k and B,

$$U_k = |i\rangle\langle j|_{A_k} \otimes \hat{a}_B + |j\rangle\langle i|_{A_k} \otimes \hat{a}_B^\dagger + |i\rangle\langle i|_{A_k} \otimes |N\rangle\langle N|_B + |j\rangle\langle j|_{A_k} \otimes |1\rangle\langle 1|_B + \sum_{r \neq i,j} |r\rangle\langle r|_{A_k} \otimes \mathbb{I}_B. \tag{4.3.2}$$

Clearly, this unitary acted upon the initial joint state $\rho_{A_k} \otimes |m\rangle\langle m|_B$ extracts $\hbar\omega \geq 0$ amount of work into the battery system with probability p_i, and $-\hbar\omega$ with probability p_j, while the expectation value of energy extracted is given by the difference in expected energy in the battery system, $\langle W \rangle = \hbar\omega(p_i - p_j) > 0$.

Now, similarly, consider the initial state $\rho_{A_1} \otimes \cdots \otimes \rho_{A_m} \otimes |m\rangle\langle m|_B$, and the unitary transformation $U_m \cdots U_1$. In the k-th step, the unitary U_k raises (denoted by a random variable x_k taking on the value $x_k = 1$), lowers ($x_k = -1$) or leave unchanged ($x_k = 0$) the battery state with certain probabilities. This operation can be represented with a string $x = x_1 \cdots x_m$

numbers, where for all $k = 1, \cdots, m$,

$$p(x_k = c) = \begin{cases} p_i & (c = 1); \\ p_j & (c = -1); \\ 1 - p_i - p_j & (c = 0). \end{cases} \tag{4.3.3}$$

The total amount of work extracted in this process is equal to $W_T = x_T \hbar\omega$, where $x_T = \sum_{i=1}^{m} x_i$, while the expectation value of x_T is $\langle x_T \rangle = m(p_i - p_j) > 0$. Since $x_1, \cdots, x_m$ are i.i.d. random variables with bounded values between -1 and 1, we can invoke Lemma 4.1 for some small number $\alpha > 0$, obtaining

$$P[x_T \leq \langle x_T \rangle - \alpha m] \leq P[|x_T - \langle x_T \rangle| \geq \alpha m] \leq \exp\left(\frac{-2\alpha^2 m^2}{\sum_{i=1}^{m} 2^2}\right) = \exp\left(\frac{-\alpha^2 m}{2}\right) = \varepsilon, \tag{4.3.4}$$

Therefore, we conclude that $W_T \geq (\langle x_T \rangle - \alpha m)\hbar\omega > 0$ except with probability ε. For any $\varepsilon > 0$ that we want to achieve, picking some small parameter $\alpha > 0$ and $m = \lceil \frac{2}{\alpha^2} \ln \frac{1}{\varepsilon} \rceil$ suffices. □

Theorem 4.2. *Given a fixed Hamiltonian $\hat{H}$, if ρ' is not the Gibbs state corresponding to a certain inverse temperature β, then for any $\varepsilon > 0$, there exists $n \in \mathbb{N}$ such that given n copies of ρ', it is possible to extract a non-zero amount of work, except with failure probability ε.*

Proof. The proof comes from a straightforward realization that any such ρ' is not *completely* passive, hence there exists some positive integer a such that $\rho'^{\otimes a}$ is non-passive. One can then invoke Theorem 4.1 with $\rho = \rho'^{\otimes a}$. For any $\varepsilon > 0$, pick some small α and $n = a \cdot m = a \cdot \frac{2}{\alpha^2} \cdot \ln \frac{1}{\varepsilon}$ suffices. □

Theorem 4.2 provides ample justification of using the set of Gibbs states of a fixed inverse temperature β as free states. We summarize this as the zeroeth law of thermodynamics:

- **Zeroeth law:** *Let $\mathscr{S}_\beta = \{(\tau_R^\beta, \hat{H}_R) \mid \tau_R^\beta = e^{-\beta \hat{H}_R}/Z_R\}$. If any $(\rho, \hat{H}_R) \notin \mathscr{S}_\beta$ is allowed as a free state, then under the full set of energy-preserving unitaries, all state transitions are possible, and the resource theory of thermal operations becomes trivial.*

We thus see that the ordinary zeroeth law is replaced by the following fact: if our class of operations includes energy conserving operations and the ability to add an arbitrary number of copies of some state ρ corresponding to any Hamiltonian $\hat{H}_R$, then the only type of state-Hamiltonian pairs $(\rho_R, \hat{H}_R)$ which does not make for a trivial theory (in the sense that all state transformations become possible), is if $\rho_R = \tau_R^\beta$, where τ_R^β is the thermal state [91] with respect to $\hat{H}_R$.

From this perspective, we now see that one can define an equivalence relation on $\mathscr{S}_\beta$ which gives for us the notion of temperature. To see this, note that given any two systems R_1, R_2 without any interaction terms between their Hamiltonians, the thermal state of the joint system (for some β) is simply the tensor product of thermal states (for the same β) for

the individual systems. Since the thermal state is uniquely defined, one may conclude that a state-Hamiltonian pair $(\rho_{R_1}\otimes\rho_{R_2},\hat{H}_{R_1}\otimes\hat{H}_{R_2})\in\mathscr{S}_\beta$ for some value of β, if and only if both $(\rho_{R_1},\hat{H}_{R_1}),(\rho_{R_2},\hat{H}_{R_2})\in\mathscr{S}_\beta$ as well.

We say that $(\rho_{R_1},\hat{H}_{R_1})\sim(\rho_{R_2},\hat{H}_{R_2})$ are equivalent free states iff the joint state is also a free state. From the above, we see that these state-Hamiltonian pairs are equivalent iff they have the same temperature with each other, and are in thermal equilibrium. We also see that such an equivalence relation is transitive, i.e. if $(\rho_{R_1},\hat{H}_{R_1})\sim(\rho_{R_2},\hat{H}_{R_2})$, and similarly $(\rho_{R_2},\hat{H}_{R_2})\sim(\rho_{R_3},\hat{H}_{R_3})$, then $(\rho_{R_1},\hat{H}_{R_1})\sim(\rho_{R_3},\hat{H}_{R_3})$.

4.4. SECOND LAWS: CATALYTIC NOISY OPERATIONS

It is instructive to first consider the case of noisy operations, where the Hamiltonian is trivial ($\hat{H}_S=\mathbb{1}_S$), and thermodynamics is reduced to the scenario of information non-equilibrium.

4.4.1. TRUMPING CONDITIONS

As we mentioned in Section 3.2.1, the condition that governs state-to-state transitions via NOs is majorization. However, we now want to analyze how the condition changes if we allow catalytic transitions. Such transitions are called catalytic noisy operations, and state transition conditions are governed by *trumping* [134], i.e. we say that a probability vector x can be trumped into y (we denote this as $x\succ_T y$) if there exists some finite-dimensional z such that

$$x\otimes z\succ y\otimes z. \tag{4.4.1}$$

The condition that z be finite-dimensional is physically reasonable, since the experimenter is working within a finite volume and below some maximum energy.

In [133] it was for the first time shown that majorization conditions are a strict subset of trumping conditions. This implies that there exists examples where originally forbidden transitions can be made possible by using a catalyst.

Example 4.1. *Consider the following example of states ρ,ρ' with ordered eigenvalues:*

$$p=\mathrm{eig}(\rho)=\left(\frac{1}{2},\frac{1}{4},\frac{1}{4},0\right), \tag{4.4.2}$$

$$p'=\mathrm{eig}(\rho')=\left(\frac{4}{10},\frac{4}{10},\frac{1}{10},\frac{1}{10}\right). \tag{4.4.3}$$

Note that $p_1>p'_1$ but $p_1+p_2<p'_1+p'_2$, therefore $p\not\succ p'$. However, consider using the catalyst ω such that $r=\mathrm{eig}(\omega)=\left(\frac{6}{10},\frac{4}{10}\right)$. Then we see that $p\otimes r\succ p'\otimes r$, so $p\succ_T p'$.

What do the trumping conditions look like? Firstly, let us note the following: consider any Schur concave function f that is additive under tensor product, i.e. $f(x\otimes z)=f(x)+f(z)$. Then if $x\succ_T y$, even if $x\not\succ y$, $f(x)\leq f(y)$ must still hold. Refs. [134, 135] independently provided necessary and sufficient conditions for x to be trumped into y, in terms of explicit subsets of all possible Schur concave functions. These functions are closely related to the Rényi entropies. We present here a set of conditions, equivalent to the Klimesh-Turgut ones, written in terms of Rényi divergences w.r.t. the uniform distribution η. Let us first state the result of Klimesh's work in the following lemma.

Lemma 4.2 (Theorem 2, [134]). *Let $x, y \in V(k)$ be k-dimensional probability vectors where $x^{\downarrow} \neq y^{\downarrow}$, and at least one of the vectors have full rank, i.e.* $\max(\text{rank}(x), \text{rank}(y)) = k$. *Then x can be trumped into y if, and only if, for all $\alpha \in (-\infty, \infty)$:*

$$f_\alpha(x) > f_\alpha(y), \tag{4.4.4}$$

where

$$f_\alpha(x) = \begin{cases} \ln \sum_{i=1}^k x_i^\alpha & (\alpha > 1); \\ \sum_{i=1}^k x_i \ln x_i & (\alpha = 1); \\ -\ln \sum_{i=1}^k x_i^\alpha & (0 < \alpha < 1); \\ -\sum_{i=1}^k \ln x_i & (\alpha = 0); \\ \ln \sum_{i=1}^k x_i^\alpha & (\alpha < 0). \end{cases} \tag{4.4.5}$$

4

Subsequently, we use Lemma 4.2 to prove that when x is only required to trump y up to some arbitrarily high precision[3], then the conditions originally stated in Lemma 4.2 can be equivalently written in terms of non-strict inequalities.

Proposition 4.1. *Let $x, y \in V(k)$ be probability vectors. Then the following conditions are equivalent:*

1. *For any $\varepsilon > 0$, there exists another vector y_ε such that $d(y, y_\varepsilon) \leq \varepsilon$ and x can be trumped into y_ε.*
2. *The following inequality holds for all $\alpha \in (-\infty, \infty)$:*

$$D_\alpha(x||\eta) \geq D_\alpha(y||\eta), \tag{4.4.6}$$

with $\eta = (1/k, \ldots, 1/k)$ being the uniform distribution.

Proof. Let us first consider the trivial case where $x^{\downarrow} = y^{\downarrow}$. Then Condition 1 holds, since for any $\varepsilon > 0$, we can define $y_\varepsilon = y$ itself, and we know that $x \succ y$ is true if $x^{\downarrow} = y^{\downarrow}$. Condition 2 also holds by definition.

Next, we divide the proof into two parts:
"Condition 1 implies 2": Let us first note that without loss of generality we can assume that y_ε is of full rank, thus relaxing the requirement in Lemma 4.2. If it is not, we can perturb the state to add a small amount of noise , obtaining $\tilde{y}_{\varepsilon'}$ which has full rank, i.e. no zeros, and satisfies $d(\tilde{y}_{\varepsilon'}, y) \leq \varepsilon'$, with ε' being arbitrarily small. With this assumption, the condition of numbers of zeroes in x and y need not be stated.

Let us then look at the case where if $x^{\downarrow} \neq y^{\downarrow}$. Assume that Condition 1 holds. Then by Lemma 4.2 we know that for any $\varepsilon > 0$, there exists y_ε such that for all $\alpha \in (-\infty, \infty)$,

$$f_\alpha(x) > f_\alpha(y_\varepsilon). \tag{4.4.7}$$

We also know that the functions f_α are continuous, and this is true even for the case when the functions diverge to infinity. For example, consider y which does not have full rank,

[3] This means that x trumps another state y_ε such that y_ε is arbitrarily close to y in terms of trace distance.

$\lim_{\varepsilon\to 0+} f_0(y_\varepsilon) = \infty$ even if y_ε is assumed to be of full rank. Therefore, we conclude that Eq. (4.4.7) implies that $f_\alpha(y) = \lim_{\varepsilon\to 0^+} f_\alpha(y_\varepsilon) \leq f_\alpha(x)$.

Note that all the functions f_α, excluding $\alpha = 0$ are proportional to $-H_\alpha(x)$. In turn, the Rényi entropy is related to $D_\alpha(x\|\eta)$ by Eq. (2.3.19). Since D_0 is obtained by taking D_α in the limit of $\alpha \to 0^+$, according to Remark 4.1 we have that $D_0(x\|\eta) \geq D_0(y\|\eta)$.

"Condition 2 implies 1": Now, suppose that Condition 2 holds instead. From the argument above we know that this translates to $f_\alpha(x) \geq f_\alpha(y)$ for all $\alpha \neq 0$. For any $\varepsilon > 0$, define

$$y_\varepsilon = (1-\varepsilon)y + \varepsilon\eta. \tag{4.4.8}$$

Then, we know that $y \succ y_\varepsilon$, which also means that $y \succ_T y_\varepsilon$. Hence by Lemma 2.2, $\forall \alpha \neq 0$, $f_\alpha(x) > f_\alpha(y_\varepsilon)$.

Before we proceed, note that for any $\varepsilon > 0$, $f_0(y_\varepsilon) < \infty$ for y_ε defined in Eq. (4.4.8). If x has full rank, then it can be verified that

$$-\frac{1}{k}\sum_{i=1}^{k} \ln x_i - \ln k = \lim_{\alpha\to 0^+} \frac{1-\alpha}{\alpha} D_\alpha(x\|\eta). \tag{4.4.9}$$

We can now analyse the following cases.
A) x is not of full rank: In this case, $f_0(x) = \infty > f_0(y_\varepsilon)$, so the condition on f_0 holds trivially.
B) x is of full rank: In this case, Eq. (4.4.9) holds. Therefore we know that if Condition 2 implies $D_0(x\|\eta) \geq D_0(y\|\eta)$, then this also implies that $f_0(x) \geq f_0(y) > f_0(y_\varepsilon)$. This independently verifies that Condition 2 implies that the Klimesh conditions for trumping corresponding to $\alpha = 0$ is satisfied.

By combining the analysis for $\alpha \neq 0$ and $\alpha = 0$, we see that assuming Condition 2 holds, we can construct y_ε such that the Klimesh trumping conditions in Lemma 4.2 holds for x and y_ε. Therefore by Lemma 4.2 implies that for any $\varepsilon > 0$, there exists y_ε such that $x \succ_T y_\varepsilon$ (Condition 1). This concludes the proof.

□

Remark 4.1. *Since the Rényi entropies are continuous in α, one can remove any discrete number of trumping conditions, as they are obtained in the limit from the other conditions.*

Recall that noisy operations is a special case of thermal operations, when the Hamiltonians involved are fully degenerate. Proposition 4.1 therefore hints at how the conditions for thermodynamics should look: for the existence of a β-catalytic thermal operation, the state transition conditions should be expressed in terms of the Rényi divergences, where the maximally mixed state should be replaced by the Gibbs thermal state of inverse temperature β. In the next Section 4.5, we will prove that this is indeed the case.

4.4.2. INVESTING A SMALL AMOUNT OF EXTRA WORK

The Klimesh-Turgut conditions in Lemma 4.2, which we have used in the derivation of Proposition 4.1, have a peculiar feature. If both $\text{rank}(x), \text{rank}(y) < k$, then we have to truncate some zeros (reducing the dimension) and compute the conditions on smaller vectors. However, the rank is also a quantity which is unstable under small perturbations. If we

slightly perturb y so that we remove zeros, then this truncate becomes unnecessary. Also, only the functions f_α corresponding to negative values of α matter under such a perturbation, as for positive α the functions $D_\alpha(x||\eta)$ do not depend on additional zeros, while the functions with negative α diverge to infinity, whenever the state is not of full rank. It is therefore desirable to eliminate such an instability on the trumping conditions.

We first note that in an earlier work, Aubrun and Nechita [140] gave conditions for trumping, in which only H_α with $\alpha > 1$ were needed (and therefore such an instability dissapears). This is because they considered a special kind of closure, where one is allowed to add an arbitrary number of zeros to the initial vector x while returning an (arbitrarily good) approximation of the targeted output y. However, the usage of such a state is not justified for a thermodynamic setting. This is because in [140], a pure ancilla is added and returned it with arbitrary small error (in trace distance), but the dimension of the ancilla needs to grow in order to make the error smaller. According to Theorem 2.1, the amount of entropy created in this process can be non-negligible. Hence, one can view the elimination of certain state transition conditions as a consequence of secretly smuggling into the process a resource with high informational non-uniformity (in other words, purity), without properly accounting for its usage. Nevertheless, one may use this as an inspiration, to justify the elimination of a subset of the second laws derived in Proposition 4.1.

In this section, by using a similar approach as in [140], we show that if we are allowed to invest a small amount of purity, then only the conditions with $\alpha \geq 0$ are relevant. We analyze the following three cases individually: (i) $\mathrm{rank}(x) < \mathrm{rank}(y)$, (ii) $\mathrm{rank}(x) > \mathrm{rank}(y)$, and (iii) $\mathrm{rank}(x) = \mathrm{rank}(y)$.

In Case (i), after truncation, x will still have zero elements, and so the Rényi divergences $D_\alpha(x\|\eta)$ with negative α will be infinite, while $D_\alpha(y\|\eta)$ will be finite. Therefore the conditions with negative α are always satisfied trivially.

In Case (ii) the transition cannot be realized, but this is already reported by comparing ranks, which can be obtained using $H_0 = \lim_{\alpha\to 0^+} H_\alpha$. This implies that the impossibility of the transition has already been reported by the conditions with $\alpha \geq 0$, and therefore the conditions stated by $\alpha < 0$ are irrelevant.

Finally, in Case (iii), if $\mathrm{rank}(x) = \mathrm{rank}(y)$, we may consider two different methods of eliminating the negative α conditions.

(A) USING AN ADDITIONAL SYSTEM WITH LARGE DIMENSION AND THE CONSUMPTION OF AN ARBITRARILY SMALL AMOUNT OF FREE ENERGY

Consider the joint transition:

$$x \otimes w_{d+1} \otimes \eta_d \to y \otimes w_d \otimes \eta_{d+1}, \tag{4.4.10}$$

where w_d is the vector corresponding to eigenvalues of a state ω_d:

$$\mathrm{eig}(\omega_d) = w_d = \underbrace{(1, 0, \ldots, 0)}_{d}. \tag{4.4.11}$$

In other words, ω_d is a pure state on a d-dimensional Hilbert space. On the other hand, the vector $\eta_d = \mathrm{eig}(\mathbb{1}_d/d)$ stands for the uniform distribution with d elements. If one quantifies the amount of work invested by the change in free energy $F(w_{d+1} \otimes \eta_d) - F(w_d \otimes \eta_{d+1})$,

then the amount of work is equal to $\ln \frac{d+1}{d}$ (assuming a trivial Hamiltonian on the system, and inverse temperature $\beta = 1$), hence it is arbitrary small in the limit of large d. Now, on the left hand side, we have more zeros than on the other side (as initially, we had the same number of zeros). Therefore, we are back to Case (i).

(B) ALLOWING APPROXIMATE TRANSITIONS AND USING AN ADDITIONAL QUBIT
Instead of insisting on preparing the exact output state, we may also eliminate the negative α conditions by allowing for the preparation of an ε-approximation, with arbitrary accuracy (as discussed in Prop. 4.1). Therefore, in Case (iii), we can also add to both sides an ancilla in w_d, a pure state of the same dimension d. Any positive integer $d > 1$ would suffice, for example we could take a qubit, i.e. $d = 2$. Both $x \otimes w_2$ and $y \otimes w_2$ will then have the same number of zeros. If we are interested in obtaining an output state which is only ε-close to the ideal output, in particular such a output state could be of full rank, so that we fall into Case (i). Then by Proposition 4.1, the transition is governed solely by the conditions with $\alpha \geq 0$. The returned state of ancilla is now only approximately pure, but the accuracy can be made arbitrarily good. Furthermore, the dimension is bounded, and hence the amount of entropy/free energy change in the process is also arbitrarily small. One can also choose the approximation in such a way that it affects only the ancilla; the original output state is not changed and will be produced exactly.

4.5. SECOND LAWS FOR EXACT CATALYSIS ON BLOCK-DIAGONAL STATES

We now turn to the case of the full theory of thermodynamics, where we have an interplay between energy and information. In this case, the Hamiltonians of the system and reservoir may be fully general. Firstly, we begin in Section 4.5.1 by showing that whenever the initial state of the system ρ_S is already block-diagonal in the energy eigenbasis of $\hat{H}_S$, it suffices to consider catalysts which are block-diagonal with respect to its Hamiltonian $\hat{H}_C$.

To derive the conditions for state transformations, we need a generalization of the majorization condition, known as d-majorization, which we describe in Section 4.5.2. This is a criterion that takes into account not only the state, but also that of the involved Hamiltonian. We derive the catalytic version of this, summarized as Theorem 4.3 in Section 4.5.4.

Finally, by using the above results, we apply our results to the case of catalytic thermal operations, to derive the generalized second laws. This is summarized in Section 4.5.5.

4.5.1. BLOCK-DIAGONAL CATALYSTS ARE SUFFICIENT

Here we will show that if the initial and final states of the system ρ_S^0, ρ_S^1 are block-diagonal w.r.t. $\hat{H}_S$, then the diagonal elements of the output state ρ_S^1 will not depend on coherences of the catalyst ρ_C^0 (between different energy levels), but only on block-diagonal elements [4]. This means that in such cases, we can replace the catalyst with its dephased version. The conditional probabilities form the channel, which maps the initial diagonal elements of the state to the final diagonal elements.

[4] In order to avoid notational clashes in the proof, instead of using ρ_S, ρ_S' to denote initial and final states, in this section we use ρ_S^0, ρ_S^1.

Let us first recall that by saying a state ρ_S is block-diagonal, we mean that there exists an eigenbasis of $\hat{H}_S$, where ρ can be written as

$$\rho = \sum_{e_S} \sigma_{e_S} |e_S\rangle\langle e_S|. \tag{4.5.1}$$

We denote such a common eigenbasis as $\{|e_S\rangle\}_{e_S}$, where $|e_S\rangle = |E_S, i_S\rangle$ is an eigenvector of $\hat{H}_S$ corresponding to eigenvalue E_S, and the index i_S runs over the degeneracy of E_S.

Let us first write out the joint initial state as

$$\rho^0_{RSC} = \rho^0_R \otimes \rho^0_S \otimes \rho^0_C, \tag{4.5.2}$$

where ρ^0_R is the heat bath, which is by definition block-diagonal. The system ρ^0_C is the state of an arbitrary catalyst, and ρ^0_S is the state of the system which we assume to be block-diagonal[5]. We then act with an energy-preserving unitary U and get the output state

$$\rho^1_{RSC} = U\rho^0_{RSC}U^\dagger. \tag{4.5.3}$$

To proceed, let us use the shorthand notation $|\mathbf{E}_{RSC}\rangle = |e_R, e_S, e_C\rangle$, and $|e_R\rangle = |E_R, i_R\rangle$ where E_R denotes energy eigenvalues and i_R denotes corresponding degeneracies for system R, likewise for system S and C. We now compute the diagonal elements of ρ^1_S:

$$\langle e_S|\rho^1_S|e_S\rangle = \langle e_S|\,\mathrm{tr}_{RC}(\rho^1_{RSC})|e_S\rangle = \sum_{e_R,e_C} \langle \mathbf{E}_{RSC}|\rho^1_{RSC}|\mathbf{E}_{RSC}\rangle, \tag{4.5.4}$$

The identity operator can be expanded as a sum

$$\mathbb{1}_{RSC} = \sum_{e_R,e_S,e_C} |\mathbf{E}_{RSC}\rangle\langle\mathbf{E}_{RSC}|. \tag{4.5.5}$$

Therefore, the diagonal elements of ρ^1_S can be written as

$$\langle E_S|\rho^1_S|E_S\rangle \tag{4.5.6}$$

$$= \sum_{e_R,e_C} \langle \mathbf{E}_{RSC}|U\rho^0_{RSC}U^\dagger|\mathbf{E}_{RSC}\rangle \tag{4.5.7}$$

$$= \sum_{e_R,e_C} \langle \mathbf{E}_{RSC}|U\mathbb{1}_{RSC}\rho^0_{RSC}\mathbb{1}_{RSC}U^\dagger|\mathbf{E}_{RSC}\rangle \tag{4.5.8}$$

$$= \sum_{e_R,e_C} \sum_{\substack{e'_R,e'_C,e'_S \\ e''_R,e''_C,e''_S}} \langle \mathbf{E}_{RSC}|U|\mathbf{E}_{R'S'C'}\rangle \times \langle \mathbf{E}_{R'S'C'}|\rho^0_{RSC}|\mathbf{E}_{R''S''C''}\rangle \times \langle \mathbf{E}_{R''S''C''}|U^\dagger|\mathbf{E}_{RSC}\rangle. \tag{4.5.9}$$

We may make use of the fact that ρ^0_R and ρ^0_S is diagonal. This means that

$$\langle \mathbf{E}_{R'S'C'}|\rho^0_{RSC}|\mathbf{E}_{R''S''C''}\rangle = \delta_{e'_R e''_R}\delta_{e'_S e''_S}\langle \mathbf{E}_{R'S'C'}|\rho^0_{RSC}|\mathbf{E}_{R''S''C''}\rangle, \tag{4.5.10}$$

[5] Furthermore, note that we may, without loss of generality assume that ρ^0_S and ρ^1_S are diagonal in the same Hamiltonian eigenbasis. This is because even if that is not the case, one may first consider the transition $\rho^0_S \to \rho^{1a}_S$, where ρ^{1a}_S has exactly the same eigenvalues as that of ρ^1_S, but is diagonal in a different Hamiltonian eigenbasis. However, one can always go from $\rho^{1a}_S \to \rho^1_S$ by implementing a unitary transformation in the corresponding degenerate energy subspace, which is a valid thermal operation.

where δ_{XY} is the Kronecker-delta function. Therefore, Eq. (4.5.9) reduces to

$$\sum_{e_R,e_C}\sum_{\substack{e'_R,e'_C,e'_S\\ e''_C}} \langle \mathbf{E}_{RSC}|U|\mathbf{E}_{R'S'C'}\rangle \times \langle \mathbf{E}_{R'S'C'}|\rho^0_{RSC}|\mathbf{E}_{R'S'C''}\rangle \times \langle \mathbf{E}_{R'S'C''}|U^\dagger|\mathbf{E}_{RSC}\rangle. \tag{4.5.11}$$

Since U preserves energy, we have more constraints on the summation: $E_R + E_S + E_C = E'_R + E'_S + E'_C$ as well as $E_R + E_S + E_C = E'_R + E'_S + E''_C$. This implies that $E'_C = E''_C$, and therefore only the terms $\langle e'_C|\rho^0_C|e''_C\rangle$ where $E'_C = E''_C$ remain. This implies, therefore, that it is sufficient to consider a catalyst ρ^0_C which is already block-diagonal.

4.5.2. A GENERALIZATION OF MAJORIZATION: $\bar{D}$-MAJORIZATION

A generalization of the majorization relation, and its relation to bistochastic operators was developed in [141] in general for continuous probability density functions, which we may specialize here for discrete probability distributions.

Definition 4.2. *Given probability vectors p,q,p',q', we say that (p,q) $\bar{D}$-majorizes (p',q') if and only if for any convex function g,*

$$\sum_i q_i g\left(\frac{p_i}{q_i}\right) \geq \sum_i q'_i g\left(\frac{p'_i}{q'_i}\right). \tag{4.5.12}$$

We denote this as $\bar{D}(p||q) \succ \bar{D}(p'||q')$.

We have already seen the application of Birkhoff-von Neumann theorem in Theorem 2.3, which relates majorization to transition between states. The next Lemma 4.3 was shown in [141] to be a extension of Theorem 2.2 from majorization to $\bar{D}$-majorization.

Lemma 4.3 (Theorem 2, [141])**.** *For probability distributions p,q,p',q', the following two conditions are equivalent:*

(i) The vector pair (p,q) $\bar{D}$-majorizes (p',q'),

$$\bar{D}(p||q) \succ \bar{D}(p'||q'). \tag{4.5.13}$$

(ii) There exists a channel Λ such that

$$\Lambda(p) = p', \quad \Lambda(q) = q'. \tag{4.5.14}$$

In fact it has been shown that a particular limited set of convex functions is sufficient. In the case when $q = q'$, the conditions can be expressed by the so-called *thermo-majorization* diagrams identified in [91]. The thermo-majorization diagrams can be easily extended also to the case $q \neq q'$, although this is not relevant for our application to thermodynamics in which $q = q'$ are the probabilities corresponding to the Gibbs state.

Lemma 4.3 implies Theorem 2.3, by taking $q = q' = \eta$ and noting that [141]

$$p \succ p' \quad \leftrightarrow \quad \bar{D}(p\|\eta) \succ \bar{D}(p'\|\eta). \tag{4.5.15}$$

A natural question is whether there is a trumping analogue for $\bar{D}$-majorization. We show that this is the case in Section 4.5.4, where we prove an extended version of Lemma 4.3 which allows catalysis. We recover analogous relations to those in Proposition 4.1. We summarize all the different scenarios in Table 4.1.

	standard majorization	$\bar{D}$-majorization
No catalysis	$\bar{D}(p\|\eta) \succ \bar{D}(p'\|\eta)$	$\bar{D}(p\|q) \succ \bar{D}(p'\|q')$
	$\exists\Lambda:\ \Lambda(p)=p',\quad \Lambda(\eta)=\eta$	$\exists\Lambda:\ \Lambda(p)=p',\quad \Lambda(q)=q'$
	$\forall_l \sum_{i=1}^{l} p_i \geq \sum_{i=1}^{l} p'_i$	comparing diagrams (for example Fig. 4.2)
With catalysis		(see Section 4.5.4)
	$D_\alpha(p\|\eta) \geq D_\alpha(p'\|\eta),\ \forall\alpha\geq 0$	$D_\alpha(p\|q) \geq D_\alpha(p'\|q'),\ \forall\alpha\geq 0$
	$\exists\Lambda, r:\ \Lambda(p\otimes r)=p'_\varepsilon\otimes r,$ $\Lambda(\eta\otimes\tilde{\eta})=\eta\otimes\tilde{\eta}$	$\exists\Lambda, r,s:\ \Lambda(p\otimes r)=p'_\varepsilon\otimes r,$ $\Lambda(q\otimes s)=q'\otimes s$

Table 4.1: Partial orderings as criteria for state transformations. The vector p'_ε is a distribution ε-close to p'.

4.5.3. NOTATIONS AND TECHNICAL TOOLS

Before setting out to prove the main result in Section 4.5.4, we develop several technical tools and lemmas that will be used in the proof.

We will start by describing an embedding channel, which will be used later to prove the above results. Consider the probability vector $p=(p_1,\cdots,p_k)$ and a vector d consisting of natural numbers $d=(d_1,\cdots,d_k)$, and let $N=\sum_{i=1}^{k} d_i$. We define the embedding

$$\Gamma_d(p)=\bigoplus_{i=1}^{k} p_i\eta_{d_i}, \tag{4.5.16}$$

More clearly, the image is the following N-dimensional probability distribution:

$$\Gamma_d(p)=\Bigg(\underbrace{\frac{p_1}{d_1},\ldots,\frac{p_1}{d_1}}_{d_1},\underbrace{\frac{p_2}{d_2},\ldots,\frac{p_2}{d_2}}_{d_2},\ldots,\ldots,\underbrace{\frac{p_k}{d_k},\ldots,\frac{p_k}{d_k}}_{d_k}\Bigg). \tag{4.5.17}$$

The inverse map Γ_d^* acts on the space of N-dimensional probability distributions $\tilde{p}$, where

$$\tilde{p}=\bigoplus_{i=1}^{k}\tilde{p}^{(i)}, \tag{4.5.18}$$

with each $\tilde{p}^{(i)}=\{\tilde{p}_1^{(i)},\cdots,p_{d_i}^{(i)}\}$ being an unnormalized, d_i-dimensional vector. The map Γ_d^* can be written as

$$\Gamma_d^*(\tilde{p})=r, \tag{4.5.19}$$

with $r = \{r_i\}_{i=1}^k$ being a normalized probability distribution, each element $r_i = \sum_{j=1}^{d_i} \tilde{p}_j^{(i)}$. The maps Γ_d and Γ_d^* are channels, and for all probability distributions p we have $\Gamma_d^*(\Gamma_d(p)) = p$. Moreover, consider the specific state vector $\gamma_d = \left(\frac{d_1}{N}, \frac{d_2}{N}, \ldots, \frac{d_k}{N}\right)$, and note that $\sum_{i=1}^k \frac{d_i}{N} = N \cdot \frac{1}{N} = 1$, and therefore γ_d is normalized. Then, we have

$$\Gamma_d(\gamma_d) = \eta_N, \tag{4.5.20}$$

is the uniform N-dimensional distribution.

In Lemmas 4.4-4.6, we develop certain properties of this embedding channel. Lemma 4.4 relates the Rényi divergence $D_\alpha(p\|q)$ to $D_\alpha(\Gamma_d(p)\|\Gamma_d(q))$. Lemma 4.5 is a technical tool that enables us to work with distributions containing irrational probability values, by introducing small corrections such that we need only to consider rational values. Lastly, Lemma 4.6 shows us when a channel can be writen as a direct sum of two channels acting disjointly on partitions of the total input/output space. These tools will later contribute to the establishment of Theorem 4.3, which is the main technical result we use to develop state transition conditions via catalytic thermal operations.

Lemma 4.4. *Let $p \in V(k)$ be an ordered, k-dimensional probability distribution, and let γ_d be the k-dimensional probability vector consisting of rational-valued elements:*

$$\gamma_d = \left(\frac{d_1}{N}, \ldots, \frac{d_k}{N}\right), \tag{4.5.21}$$

where $d = (d_1, \cdots, d_k)$ is a vector where each element $d_i \in \mathbb{N}$ is a natural number. Define the following fine-grained, N-dimensional probability distribution

$$\tilde{p} = \Gamma_d(p) = \Bigg(\underbrace{\frac{p_1}{d_1}, \ldots, \frac{p_1}{d_1}}_{d_1}, \underbrace{\frac{p_2}{d_2}, \ldots, \frac{p_2}{d_2}}_{d_2}, \ldots, \ldots, \underbrace{\frac{p_k}{d_k}, \ldots, \frac{p_k}{d_k}}_{d_k}\Bigg). \tag{4.5.22}$$

Then for $\alpha \in [-\infty, \infty]$ we have

$$D_\alpha(p||\gamma_d) = D_\alpha(\tilde{p}||\eta_N), \tag{4.5.23}$$

with $\eta_N = (1/N, \ldots, 1/N)$ being the uniform distribution. By Eq. (4.5.20), this means that

$$D_\alpha(p||\gamma_d) = D_\alpha(\Gamma_d(p)||\Gamma_d(\gamma_d)). \tag{4.5.24}$$

Proof. Let us first assume that $\alpha \notin \{-\infty, 0, 1, \infty\}$. Then

$$D_\alpha(p||\gamma_d) = \frac{1}{\alpha - 1} \log \sum_{i=1}^k p_i^\alpha \left(\frac{d_i}{N}\right)^{1-\alpha} \tag{4.5.25}$$

$$= \frac{1}{\alpha - 1} \log \sum_{i=1}^k d_i \left(\frac{p_i}{d_i}\right)^\alpha \left(\frac{1}{N}\right)^{1-\alpha} \tag{4.5.26}$$

$$= \frac{1}{\alpha - 1} \log \sum_{i=j}^N \tilde{p}_j^\alpha \left(\frac{1}{N}\right)^{1-\alpha} = D_\alpha(\tilde{p}||\eta_N), \tag{4.5.27}$$

where note that in the third inequality we sum over the elements of the fine-grained distribution $\tilde{p}$, and for each $i \in \{1, \cdots, k\}$, $\tilde{p}$ contains d_i number of degenerate values $\frac{p_i}{d_i}$. For $\alpha \in \{-\infty, 0, 1, \infty\}$ one can obtain the relation by considering limits. Here we show this explicitly. For $\alpha = 0$, we have

$$D_0(p||\gamma_d) = -\log \sum_{i:p_i\neq 0} \left(\gamma_d\right)_i = -\log \sum_{j:p_j\neq 0} \frac{d_i}{N} = -\log \sum_{i:\tilde{p}_i\neq 0} \frac{1}{N} = D_0(\tilde{p}||\eta_N). \tag{4.5.28}$$

For $\alpha \to \infty$, we have

$$D_\infty(p||\gamma_d) = \log \min\left\{\lambda : \forall i, \lambda \geq \frac{p_i}{d_i/N}\right\} \tag{4.5.29}$$

$$= \log \min\left\{\lambda : \forall i, \lambda \geq \frac{p_i/d_i}{1/N}\right\} = D_\infty(\tilde{p}||\eta_N), \tag{4.5.30}$$

and similarly for $\alpha \to -\infty$. Finally, for $\alpha = 1$,

$$D_1(p||\gamma_d) = \sum_{i=1}^{k} p_i \log \frac{p_i N}{d_i} = \sum_{i=1}^{k} d_i \frac{p_i}{d_i} \log \frac{p_i N}{d_i} = D_1(\tilde{p}||\eta_N). \tag{4.5.31}$$

□

Lemma 4.5. *Given distributions $q, \tilde{q} \in V(n)$, such that the trace distance $d(q, \tilde{q}) \leq \varepsilon$. Then there exists a channel E such that $E(q) = \tilde{q}$ and for any distribution p we have that*

$$d(E(p), p) \leq \frac{\varepsilon}{\min\limits_{j:q_j>0} q_j} = \Theta(\varepsilon). \tag{4.5.32}$$

Proof. Before beginning to construct the channel E, let us define the sets $\mathscr{I}_+ = \{k : q_k \geq \tilde{q}_k\} \backslash \{k : q_k = q_k = 0\}$ and $\mathscr{I}_- = \{k : q_k < \tilde{q}_k \vee q_k = \tilde{q}_k = 0\}$, and $\varepsilon_k^+ = q_k - \tilde{q}_k$ for $k \in \mathscr{I}_+$ and $\varepsilon_k^- = \tilde{q}_k - q_k$ for $k \in \mathscr{I}_-$. Also, denote $\mathrm{span}(\mathscr{S})$ to be the probability space of an indice set $\mathscr{S}$. Note that due to normalization of distributions q and $\tilde{q}$,

$$\sum_{k\in I_+} \varepsilon_k^+ = \sum_{k\in I_-} \varepsilon_k^- = \varepsilon, \tag{4.5.33}$$

where ε is the trace distance between q and $\tilde{q}$.

Let us first consider a channel $R : \mathrm{span}(\mathscr{I}_+) \to \mathrm{span}(\mathscr{I}_-)$, i.e. the channel R acts on any probability distribution $r \in \mathrm{span}(\mathscr{I}_+)$, and the output probability vector $R(r) \in \mathrm{span}(\mathscr{I}_-)$. We will later use R as a subchannel in constructing the channel E. We define R by its transition probabilities

$$r_{k\to j} = \frac{\varepsilon_j^-}{\varepsilon}, \qquad k \in \mathscr{I}_+ \text{ and } j \in \mathscr{I}_-. \tag{4.5.34}$$

One can then observe the following:

1. To verify that R is a channel, note that each $r_{k\to j} \geq 0$ and $\sum\limits_{j\in\mathscr{I}_-} r_{k\to j} = 1$.

2. This channel R satisfies the following properties: for all $j \in \mathscr{I}_-$,

$$\sum_{k \in \mathscr{I}_+} \varepsilon_k^+ r_{k\to j} = \varepsilon_j^- . \tag{4.5.35}$$

Next, we define channel E by the following transition probabilities

$$s_{k\to j} = \begin{cases} 1 - \frac{\varepsilon_k^+}{q_k} & j = k \quad k \in \mathscr{I}_+ \\ 0 & j \neq k \quad j,k \in \mathscr{I}_+ \\ \frac{\varepsilon_k^+}{q_k} r_{k\to j} & j \in I_- \quad k \in \mathscr{I}_+ \\ 1 & j = k \quad k \in \mathscr{I}_- \\ 0 & j \neq k \quad k \in \mathscr{I}_- . \end{cases} \tag{4.5.36}$$

We note that this is a valid set of transition probabilities, by noting that since $q_k = \tilde{q}_k + \varepsilon_k^+$ and $\tilde{q}_k, \varepsilon_k^+ \geq 0$, therefore $1 - \frac{\varepsilon_k^+}{q_k} \geq 0$. Also, note that when $q_k = 0$, either 1) $k \in \mathscr{I}_-$, or 2) $\tilde{q}_k = q_k = 0$ so that one can omit the symbol for such a k altogether. The channel is presented graphically in Fig. 4.3 for the reader's convenience. One can check either from Eq. (4.5.36) or from Fig. 4.3 that E is indeed a channel.

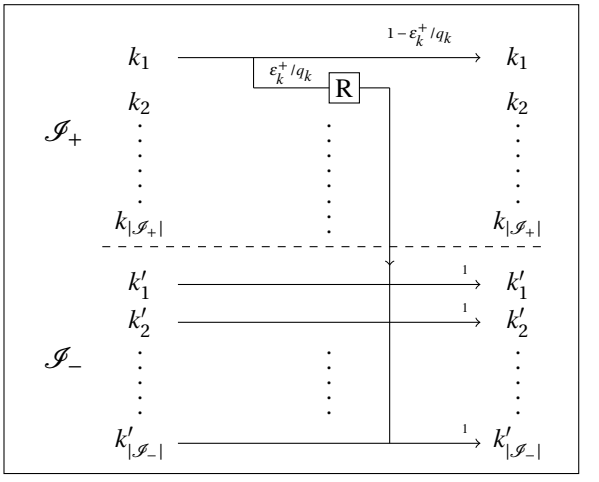

Figure 4.3: Graphical representation of the channel E.

We now verify that the channel satisfies $E(q) = \tilde{q}$. For $j \in \mathscr{I}_+$ we have

$$E(q)_j = \sum_k q_k p_{k\to j} = \sum_{k\in\mathscr{I}_+} q_k s_{k\to j} + \underbrace{\sum_{k\in\mathscr{I}_-} q_k s_{k\to j}}_{=0} \tag{4.5.37}$$

$$= \underbrace{\sum_{k\in\mathscr{I}_+, k\neq j} q_k s_{k\to j}}_{=0} + q_j s_{j\to j} \tag{4.5.38}$$

$$= q_j\left(1 - \frac{\varepsilon_j^+}{q_j}\right) = \tilde{q}_j, \tag{4.5.39}$$

while for $j \in \mathscr{I}_-$ we get

$$E(q)_j = \sum_k q_k s_{k\to j} = \sum_{k\in\mathscr{I}_+} q_k s_{k\to j} + \sum_{k\in\mathscr{I}_-} q_k s_{k\to j} \tag{4.5.40}$$

$$= \sum_{k\in\mathscr{I}_+} q_k \frac{\varepsilon_k^+}{q_k} r_{k\to j} + q_j \tag{4.5.41}$$

$$= \sum_{k\in\mathscr{I}_+} \varepsilon_k^+ r_{k\to j} + q_j = \varepsilon_j^- + q_j = \tilde{q}_j. \tag{4.5.42}$$

Finally, we consider any probability distribution p, and analyse the distance $d(E(p), p)$. Denoting $E(p) = \tilde{p}$ we get

$$\tilde{p}_j = \begin{cases} p_j\left(1 - \frac{\varepsilon_j^+}{q_j}\right), & \text{for } j \in I_+ \\ \varepsilon_j^- + p_j, & \text{for } j \in I_- \end{cases} \tag{4.5.43}$$

We know that the channel E increases the probabilities in set $\mathscr{I}_+$, and decreases those in $\mathscr{I}_-$. From Eq. (4.5.33), we also realized that the trace distance of two normalized distributions can be written as the sum of difference across only either one of the sets $\mathscr{I}_+, \mathscr{I}_-$. Therefore,

$$\frac{1}{2}\sum_j |p_j - \tilde{p}_j| = \sum_{j\in I_+} \varepsilon_j^+ \frac{p_j}{q_j} \leq \sum_{j\in I_+} \frac{\varepsilon_j^+}{q_j} \leq \frac{\varepsilon}{\min\limits_{j:q_j>0} q_j}. \tag{4.5.44}$$

This concludes the proof. □

Lemma 4.6. *Consider a channel such that for some fixed n-dimensional probability distribution $t = (t_1, \ldots, t_l, 0, \ldots 0)$ the channel gives output $t' = (t'_1, \ldots, t'_l, 0, \ldots 0)$. Moreover, $\Lambda(w) = w$ holds for some full rank distribution w. Then this channel can be decomposed as $\Lambda = \Lambda_1 \oplus \Lambda_2$, where Λ_1 acts only on the first l-elements, mapping them onto the same group of elements, while Λ_2 acts similarly on the remaining $n - l$ elements.*

Proof. Consider the joint probability of two random variables (X, Y), given by the preserved distribution w and the channel. Let $X = 0$ denote the event that the inputs are from the first group (items from 1 to l), and $X = 1$ that they are from the second group (items from $l + 1$ to n), and Y denotes similar events for the outputs. Since the channel preserves w, we have

that $P(Y=0) = P(X=0)$. Moreover, since the channel sends t into t' , this means that $p(Y=0|X=0) = 1$. We then have

$$p(Y=0) = p(Y=0|X=0)p(X=0) + p(Y=0|X=1)p(X=1) \tag{4.5.45}$$
$$= p(Y=0) + p(Y=0|X=1)p(X=1) \tag{4.5.46}$$

so that either $P(X=1)=0$ or $p(Y=0|X=1)=0$. However, since w is of full rank, we know that $P(X=1)>0$. Therefore $p(Y=0|X=1)=0$ must hold. We have therefore that $P(Y=0|X=0) = P(Y=1|X=1) = 1$ which means that the channel is direct sum of two channels, acting on two disjoint groups of elements $\{1,\cdots,l\}$ and $\{l+1,\cdots,n\}$. □

4.5.4. CATALYTIC $\bar{D}$-MAJORIZATION

In this section, we prove a crucial result (Theorem 4.3), which relates monotonicity of Rényi divergences to catalytic transformations. This can be viewed as both a generalization of trumping relations [134, 135] and the d-majorization result [141]. It also gives an operational interpretation to the Rényi divergences, answering the question posed in [60].

With the tools listed in Section 4.5.3 in place, we can now proceed to state and prove the main theorem of this section.

Theorem 4.3. *Consider the probability distributions p, p', q and q', where q and q' have full rank. Then, the following conditions are equivalent:*

(i) For all $\alpha \in (-\infty,\infty), D_\alpha(p||q) \geq D_\alpha(p'||q')$.

(ii) For any $\delta > 0$, there exists probability distributions r, s of full rank, a distribution p'_δ and a classical channel Λ such that

1. $\Lambda(p\otimes r) = p'_\delta \otimes r$,
2. $\Lambda(q\otimes s) = q'\otimes s$,
3. $d(p', p'_\delta) \leq \delta$.

Moreover, we can take $s=\eta$, η being the uniform distribution onto the support of r.

Proof. "(i) → (ii)". To prove in this direction, we suppose that Condition (i) holds, and construct a channel Λ that satisfies (ii), with some ε that can be chosen arbitrarily small.

Let us consider the following two cases separately:

(A) The probabilities in q and q' are rational. Without loss of generality, they can be written as $q = d/N$ and $q' = d'/N$ where d, d' are two vectors containing positive integers, $d = (d_1,\cdots,d_k), d' = (d'_1,\cdots,d'_k)$, such that $\sum_{i=1}^k d_i = \sum_{i=1}^k d'_i = N$.

With this, define two embedding channels Γ_d and $\Gamma_{d'}$ associated with d and d' respectively. The fine-grained distributions of p and p' are given by

$$\tilde{p} = \Gamma_d(p) = \bigoplus_{i=1}^k p_i\eta_i, \qquad \tilde{p}' = \Gamma_{d'}(p') = \bigoplus_{i=1}^k p'_i\eta'_i,$$

where η_i, η_i' are maximally mixed distributions of dimensions d_i and d_i' respectively. Condition (i) together with Lemma 4.4 tells us that

$$D_\alpha(\tilde{p}||\eta_N) = D_\alpha(p||q) \geq D_\alpha\left(p'\middle\|q'\right) = D_\alpha\left(\tilde{p}'\middle\|\eta_N\right), \tag{4.5.47}$$

and hence by Proposition 4.1, we know that for any $\varepsilon > 0$, there exists a distribution $\tilde{p}'_\varepsilon$ such that $d\left(\tilde{p}', \tilde{p}'_\varepsilon\right) \leq \varepsilon$ and $\tilde{p}$ can be trumped into $\tilde{p}'_\varepsilon$. Equivalently, there exists a probability distribution r (the catalyst) and a bistochastic map Φ such that

$$\Phi(\tilde{p} \otimes r) = \tilde{p}'_\varepsilon \otimes r. \tag{4.5.48}$$

Note that by Lemma 4.6, r can be without loss of generality be of full rank, or in other words, the zeros in r do not affect finding such a bistochastic map. More precisely, let us consider the case where r does not have full rank, but has some rank $a < \dim(r)$ instead. Then by setting $t = \tilde{p} \otimes r$, $t' = \tilde{p}'' \otimes r$ and $w = \eta_N \otimes \eta$, we can use Lemma 4.6 to show that $\Phi = \Phi_1 \oplus \Phi_2$, where the channel Φ_1 gives us

$$\Phi_1(\tilde{p} \otimes r) = \tilde{p}'' \otimes r, \quad \Phi_1(\eta_N \otimes \eta_a) = \eta_N \otimes \eta_a, \tag{4.5.49}$$

where η_a is the uniform distribution on the support of r. On the other hand if r is of full rank, then $\Phi = \Phi_1$.

Now, consider the following mapping

$$\Lambda_A = \left(\Gamma^*_{d'} \otimes \mathbb{1}\right) \circ \Phi_1 \circ (\Gamma_d \otimes \mathbb{1}). \tag{4.5.50}$$

This map Λ_A transforms $p \otimes r$ into $p'' \otimes r$, setting $\varepsilon = \delta$ satisfies Conditions 1 and 3 in (ii). To satisfy Condition 2, we want $\Lambda_A(q \otimes s) = q' \otimes s$ for some s. This is achieved by taking $s = \eta$, a uniform distribution of any dimension. Indeed, since $\Gamma_d(q) = \mathbb{1}/N$, $(\Gamma_d \otimes \mathbb{1})(q \otimes \eta)$ is also a maximally mixed distribution. Since Φ_1 is bistochastic, it preserves this distribution. Finally, by definition of $\Gamma_{d'}$ we have $\Gamma^*_{d'}(\mathbb{1}/N) = q'$.

(B) The distributions q or q' contain irrational values. We show that in such cases, a similar approach in (A) can be used, by considering distributions $\tilde{q}$ which are rational and close to the original distributions.

Note that for any real $\alpha > 0$, $D_\alpha(p\|q)$ is a continuous function of both arguments p and q, whenever q is of full rank. For $\alpha < 0$, whenever p does not have full rank, both $D_\alpha(p\|q)$ and $D_\alpha(p\|\tilde{q})$ diverge to infinity. When p has full rank, continuity can be obtained by noting that $D_\alpha(p\|q) = c \cdot D_{1-\alpha}(q\|p)$ and $D_\alpha(p\|\tilde{q}) = c \cdot D_{1-\alpha}(\tilde{q}\|p)$ for some positive c, and $1 - \alpha > 0$, hence $D_{1-\alpha}(q\|p)$ is continuous.

By Lemma 4.5, we use the channel E that maps q into $\tilde{q}$ while not perturbing p too much. More precisely, for any $\varepsilon > 0$, one can define a stochastic map E such that

$$E(q) = \tilde{q}, \quad d(\tilde{q}, q) \leq \varepsilon, \tag{4.5.51}$$

and $d(E(p), p) \leq \Theta(\varepsilon)$ for any other state p. From the above discussion, we conclude that when in the limit of $\varepsilon \to 0$, Condition 1 implies that $D_\alpha(p||\tilde{q}) \geq D_\alpha(p'||\tilde{q}')$ holds as well. More precisely, since we can choose ε to be arbitrarily small, in the limit of $\varepsilon \to 0$,

$$D_\alpha(E(p)||\tilde{q}) = D_\alpha(p||q) \geq D_\alpha(p'||q') = D_\alpha(p'||\tilde{q}'). \tag{4.5.52}$$

Following part (A) of the proof which established the result for rational q and q', we find that there is a catalyst r, a stochastic operation Λ_A and a distribution p'' such that

$$d(p'', p') \leq \varepsilon, \tag{4.5.53}$$

and

$$\Lambda_A(E(p) \otimes r) = p'' \otimes r, \quad \Lambda_A(E(q) \otimes \eta) = \tilde{q}' \otimes \eta, \tag{4.5.54}$$

with η the maximally mixed distribution.

If q' also contains irrational values, we can similarly define a second correction map that maps q' into $\tilde{q}'$ while not perturbing p'' too much. By invoking Lemma 4.5 on q', we construct E' such that

$$E'(q') = \tilde{q}', \quad \text{and for any probability distribution } p'', \; d(E'(p''), p'') \leq \Theta(\varepsilon). \tag{4.5.55}$$

Our final stochastic map is given by $E' \circ \Lambda_A \circ E$, where

$$\begin{aligned}(E' \otimes \mathbb{1}) \circ \Lambda_A \circ (E \otimes \mathbb{1})(q \otimes \eta) &= (E' \otimes \mathbb{1}) \circ \Lambda_A(\tilde{q} \otimes \eta) \\ &= (E' \otimes \mathbb{1})(\tilde{q}' \otimes \eta) \\ &= q' \otimes \eta,\end{aligned} \tag{4.5.56}$$

and

$$\begin{aligned}(E' \otimes \mathbb{1}) \circ \Lambda_A \circ (E \otimes \mathbb{1})(p \otimes r) &= (E' \otimes \mathbb{1}) \circ \Lambda_A(E(p) \otimes r) \\ &= (E' \otimes \mathbb{1})(p'' \otimes r) \\ &= E'(p'') \otimes r,\end{aligned} \tag{4.5.57}$$

such that by using Eq. (4.5.53) and (4.5.55), together with the triangle inequality for trace distance,

$$d(E'(p''), p') \leq d(p'', p') + d(E'(p''), p'') \leq \Theta(\varepsilon) =: \delta. \tag{4.5.58}$$

Since ε can be chosen arbitrarily, the first part of the theorem follows.

"(ii) → (i)". Suppose that for all $\varepsilon > 0$ there exist probability distributions r, s, p'_ε and a stochastic map Λ such that

$$d(p', p'_\varepsilon) \leq \varepsilon, \tag{4.5.59}$$

and

$$\Lambda(p \otimes r) = p'_\varepsilon \otimes r, \quad \Lambda(q \otimes s) = q' \otimes s, \tag{4.5.60}$$

and the support of s includes the support of r. Then by monotonicity of the Rényi divergences,

$$D_\alpha(p'_\varepsilon \otimes r || q' \otimes s) \leq D_\alpha(p \otimes r || q \otimes s), \tag{4.5.61}$$

which equals

$$D_\alpha(p'_\varepsilon || q') + D_\alpha(r||s) \leq D_\alpha(p||q) + D_\alpha(r||s), \tag{4.5.62}$$

by additivity. Since both r and s are full rank, $D_\alpha(r||s)$ is finite, and can be subtracted from both sides. Lastly, we consider the limit $\varepsilon \to 0$. Recall that as long as the second

argument q' has full rank, for any $\alpha > 0$, $D_\alpha(p'||q')$ is continuous w.r.t. both p' and q'. For $\alpha < 0$, whenever p' with full rank, continuity holds. If p' does not have full rank, then $\lim_{\varepsilon\to 0} D_\alpha(p'_\varepsilon\|q') = \infty = D_\alpha(p'\|q')$. Hence we obtain

$$D_\alpha(p'||q') \leq D_\alpha(p||q) \tag{4.5.63}$$

for all $\alpha > 0$ and $\alpha < 0$. Since $D_0(p\|q) = \lim_{\alpha\to 0^+} D_\alpha(p\|q)$, the above inequality holds also for $\alpha = 0$. □

4.5.5. THE SECOND LAWS FOR BLOCK-DIAGONAL STATES

In this section we formulate the state transformation conditions, namely the second laws of thermodynamics. We will first do this for states block-diagonal in the energy eigenbasis. The conditions are given in terms of generalized free energies, which are defined as follows:

$$F_\alpha(\rho,\hat{H}) := \beta^{-1}\cdot\left[\ln Z + \hat{D}_\alpha(\rho\,\|\,\tau^\beta)\right] = F(\tau_\beta,\hat{H}) + \beta^{-1}\cdot\hat{D}_\alpha(\rho\,\|\,\tau^\beta) \tag{4.5.64}$$

where Z is the partition function for the Hamiltonian $\hat{H}$, and τ^β is the thermal state[6]. Since we are analyzing the case where ρ is block-diagonal, this means that it shares a common basis with the thermal state τ^β for any $\beta \geq 0$. Recall that in Def. 2.17, this implies that $\hat{D}_\alpha(\rho\,\|\,\tau^\beta) = D_\alpha(p\|q)$, where p,q are eigenvalues of ρ,τ^β respectively. Note that F_1 is the Helmholtz free energy in Eq. (1.1.2), and that for thermal states and pure energy eigenstates, all free energies are equal to the Helmholtz quantity.

Theorem 4.4 (Second laws for block-diagonal states)**.** *Consider a system with Hamiltonian $\hat{H}_S$. Then a state ρ_S block-diagonal in the energy eigenbasis can be transformed with arbitrary accuracy into another block-diagonal state ρ'_S under catalytic thermal operations if and only if, for all $\alpha \in (-\infty,\infty)$,*

$$F_\alpha(\rho_S,\hat{H}_S) \geq F_\alpha(\rho'_S,\hat{H}_S). \tag{4.5.65}$$

Proof. We will prove it using Theorem 4.3. Consider an initial state of the system ρ_S which is block-diagonal. In Section 4.5.1, we showed the sufficiency of using a block-diagonal catalyst. Therefore, the entire initial state (system plus catalyst) is block-diagonal.

Suppose first that Eq. (4.5.65) holds for $\alpha \in (-\infty,\infty)$, for the states ρ_S and ρ'_S. By Eq. (4.5.64), this is equivalent to having

$$D_\alpha(\rho_S||\tau_S^\beta) \geq D_\alpha(\rho'_S||\tau_S^\beta). \tag{4.5.66}$$

We now need to show that one can transform the state ρ_S into another state arbitrarily close to ρ'_S by catalytic thermal operations.

Let us denote p and p' to be eigenvalues of ρ_S and ρ'_S respectively, and $q = q'$ are the eigenvalues of τ_S^β. Then, using Theorem 4.3, we get that there exists a channel Λ and uniform distribution η such that (i) Λ preserves the state $q\otimes\eta$, (ii) Λ sends $p\otimes r$ into $p'_\varepsilon\otimes r$,

[6]The main reason for defining these generalized free energies with the factor of $\beta^{-1}\ln 2$ is so that F_1 reduces exactly to the historical definition of the Helmholtz free energy.

where p'_ε approximates p'. Condition (i) means that we can take the catalyst system with trivial Hamiltonian. Thus we have

$$\Lambda(\rho_S \otimes \rho_C) = \rho_S^{\text{out}} \otimes \rho_C, \tag{4.5.67}$$

where $d(\rho_S^{\text{out}}, \rho'_S) \leq \varepsilon$ and

$$\Lambda(\tau_S^\beta \otimes \tau_C^\beta) = \tau_S^\beta \otimes \tau_C^\beta, \tag{4.5.68}$$

where τ_C^β is the maximally mixed state on catalyst system C, i.e. Λ preserves the thermal state of the system SC. However, we know that for block-diagonal state transitions, thermal operations are precisely the operations that preserve the thermal state [90, 91]. Thus the required transition can be made by catalytic thermal operations.

Conversely, let us assume that for given states ρ_S and ρ'_S there exists a CPTPM Λ, and a system C with the hamiltonian $\hat{H}_C$, and state ρ_C such that

$$\Lambda(\tau_S^\beta \otimes \tau_C^\beta) = \tau_S^\beta \otimes \tau_C^\beta, \quad \Lambda(\rho_S \otimes \rho_C) = \rho_S^{\text{out}} \otimes \rho_C. \tag{4.5.69}$$

where $d(\rho_S^{\text{out}}, \rho'_S) \leq \varepsilon$. In Sec. 4.5.1 we have shown that since the input and output states are block-diagonal, we can take the state ρ_C to be block-diagonal too, and therefore the existence of Λ is equivalent to the existence of a classical channel Λ_{cl} such that

$$\Lambda_{\text{cl}}(q \otimes s) = q \otimes s, \quad \Lambda_{\text{cl}}(p \otimes r) = p'_\varepsilon \otimes r, \tag{4.5.70}$$

Thus we can apply Theorem 4.3, obtaining that

$$D_\alpha(\rho_S \| \tau_S^\beta) \geq D_\alpha(\rho'_S \| \tau_S^\beta) \tag{4.5.71}$$

for all real α which is equivalent to Eq. (4.5.65). □

GETTING RID OF SECOND LAWS WITH NEGATIVE α

Similar to the approach in Section 4.4.2, in addition to the catalyst, we can consider borrowing some system with fixed size (e.g. a qubit) in a pure state, given that we will return it with arbitrary good fidelity. This will lift all the conditions on $\alpha < 0$.

Theorem 4.5. *Consider the case where it is allowed to borrow a qubit with a trivial Hamiltonian $\hat{H}_A = \mathbf{0}_A$, in the state $\rho_A = |0\rangle\langle 0|$, as long as it is returned ε-close in trace distance, for all $\varepsilon > 0$. Then, a state ρ_S block-diagonal in the energy eigenbasis can be transformed with arbitrary accuracy into another block-diagonal state ρ'_S if and only if for all $\alpha \geq 0$,*

$$F_\alpha(\rho_S, \hat{H}_S) \geq F_\alpha(\rho'_S, \hat{H}_S). \tag{4.5.72}$$

Proof. The forward direction of the proof is straightforward: suppose first that one can transform the state $\rho_S \otimes |0\rangle\langle 0|$ into arbitrary good version of $\rho'_S \otimes |0\rangle\langle 0|$. Then we proceed as in the proof of Theorem 4.3 using monotonicity and additivity of D_α, also noticing that D_α is finite. Thus, for all $\alpha \geq 0$, we get

$$D_\alpha(\rho_S || \tau_S^\beta) \geq D_\alpha(\rho'_S || \tau_S^\beta) \tag{4.5.73}$$

for $\alpha \geq 0$, so that by the definition of F_α in Eq. (4.5.64), which is equivalent to D_α up to a multiplicative constant and an additive constant, the conditions in Eq. (4.5.72) are satisfied.

For the opposite direction, assume that Eq. (4.5.72) is satisfied for $\alpha \geq 0$. This implies that Eq. (4.5.73) hold, and therefore for $\alpha \geq 0$,

$$D_\alpha(\rho_S \otimes |0\rangle\langle 0|_A || \tau_S^\beta \otimes \eta_A) \geq D_\alpha(\rho'_S \otimes |0\rangle\langle 0|_A || \tau_S^\beta \otimes \eta_A) \tag{4.5.74}$$

holds as well. This implies that for any value of $\varepsilon > 0$, we may consider the state $\rho'_A = (1-\varepsilon)|0\rangle\langle 0| + \varepsilon|1\rangle\langle 1|$. Then for $\alpha \geq 0$,

$$D_\alpha(\rho_S \otimes |0\rangle\langle 0|_A || \tau_S^\beta \otimes \eta_A) \geq D_\alpha(\rho'_S \otimes \rho'_A || \tau_S^\beta \otimes \eta_A) \tag{4.5.75}$$

On the other hand, note that for $\alpha < 0$, D_α is infinite on the left side of Eq. (4.5.75) (since $|0\rangle\langle 0|_A$ is not of full rank), and finite on the right for any $\varepsilon > 0$. Moreover $D_\alpha(\rho_S \otimes |0\rangle\langle 0| \, || \tau_{SC}^\beta) = D_\alpha(\rho_S \| \tau_S^\beta) + D_\alpha(|0\rangle\langle 0| \, || \tau_C^\beta)$ and same for S'. This means that Eq. (4.5.75) also holds for $\alpha < 0$ automatically. Thus we get that for all $\alpha \in \mathbb{R}$,

$$D_\alpha(\rho_S \otimes |0\rangle\langle 0|_A || \tau_S^\beta) \geq D_\alpha(\rho'_S \otimes \rho'_A || \tau_S^\beta). \tag{4.5.76}$$

Hence, by Theorem 4.4 we can transform the state $\rho_S \otimes |0\rangle\langle 0|$ into arbitrarily good approximate version of $\rho'_S \otimes |0\rangle\langle 0|$. □

In Theorem 4.5, we have borrowed a completely pure state qubit, and return it with full rank (but arbitrarily close to being pure), to get rid of the conditions for negative α. This might have raised objections, that a completely pure state is hard to obtain in the first place according to the second laws for all $\alpha \in \mathbb{R}$. However, let us note, that we might also borrow a noisy version of $|0\rangle\langle 0|_A$, namely $\rho_A^\delta = (1-\delta)|0\rangle\langle 0| + \delta|1\rangle\langle 1|$, where $\delta \ll 1$.

If $F_\alpha(\rho_S^0, \hat{H}) \geq F_\alpha(\rho_S^1, \hat{H})$ for $\alpha \geq 0$, We know from Theorem 4.5 that there exists a CTO $\mathcal{N}$ such that $\mathcal{N}(\rho_S \otimes |0\rangle\langle 0|_A) = \rho_{SA}^1 \approx_\varepsilon \rho'_S \otimes \rho'_A$. Therefore, since the trace distance is non-increasing under CPTPMs, applying

$$d(\rho_{SA}^1, \mathcal{N}(\rho_S \otimes \rho_A^\delta)) \leq d(\rho_S \otimes |0\rangle\langle 0|_A, \rho_S \otimes \rho_A^\delta) = \delta. \tag{4.5.77}$$

This implies that $\mathcal{N}(\rho_S \otimes \rho_A^\delta) \approx_{\varepsilon+\delta} \rho'_S \otimes \rho'_A$, and therefore we can still 1) return the ancilla, and 2) obtain the output state ρ_S^1 with accuracy $\varepsilon + \delta$ in trace norm. The usage of an ancilla is justified here because of the small, fixed dimension, and hence the amount of work used is also arbitrarily small. However as we will discuss in Chapter 5, if there are no further restrictions on the available catalyst, then closeness in trace distance is not a suitable demand on the returned catalyst in thermodynamic transformations.

APPLICATION: LANDAUER ERASURE WITH A QUANTUM MAXWELL DEMON

As an application of the results, we consider a special case of a Maxwell demon with a memory Q, who wants to reset a system S to some final pure state $|\psi^E\rangle\langle\psi^E|_S$ with fixed energy E. The demon's memory could initially be correlated with the system, so the joint state of demon and system is given by ρ_{SQ}. The demon wishes to reset the system S, but the local reduced state of the demon's memory should not change.

This problem can be seen as a fully quantum version of the standard Maxwell demon/Landauer erasure scenario, and has been considered in the case of a trivial Hamiltonian [107, 130] and when the Maxwell demon does not have access to ancilliary systems. The result of [107] gave a thermodynamic interpretation to the notion of negative information [142]. in the single-shot scenario with ancillas, the notion of partial information takes on a different form, which we shall now derive.

The cost of resetting the system, W_{reset}, is the minimum required amount of energy such that the transition

$$\rho_{QS} \otimes |0\rangle\langle 0| \to \rho_Q \otimes |\psi^E\rangle\langle\psi^E|_S \otimes |W_{\text{reset}}\rangle\langle W_{\text{reset}}| \tag{4.5.78}$$

is possible via catalytic thermal operations. By applying the generalized second laws, this quantity is given by

$$\begin{aligned} W_{\text{reset}} &= -\inf_{\alpha\geq 0} \beta^{-1} \cdot \left[\hat{D}_\alpha(\rho_{QS}\|\tau^\beta{}_{QS}) - \hat{D}_\alpha(\rho_Q \otimes \psi_S^E\|\tau^\beta{}_{QS})\right] \\ &= -\inf_{\alpha\geq 0} \beta^{-1} \cdot \left[\hat{D}_\alpha(\rho_{QS}\|\tau^\beta{}_{QS}) - \hat{D}_\alpha(\rho_Q\|\tau^\beta{}_{Q})\right] + E + \beta^{-1}\ln Z_S \end{aligned} \tag{4.5.79}$$

In the case when the Hamiltonian is trivial, this reduces to

$$W_{\text{reset}} = \beta^{-1} \cdot \sup_{\alpha\geq 0} \left[H_\alpha(\rho_{QS}) - H_\alpha(\rho_Q)\right] \tag{4.5.80}$$

When this quantity is negative, the demon can reset the system to a pure state, and not only does this not cost work, but the corresponding amount of work is actually gained. Finally, in the case of standard Landauer erasure of a qubit with a non-trivial Hamiltonian (where we don't have a memory and start in the thermal state), Eq. (4.5.79) gives what one expects from the macroscopic scenario, namely $W_{\text{reset}} = E + \beta^{-1}\ln Z_S$.

4.6. SECOND LAWS FOR EXACT CATALYSIS ON ARBITRARY QUANTUM STATES

For states which are not block-diagonal, the generalized free energies remain necessary conditions that govern a state transition. However, they are no longer sufficient to guarantee the possibility of transition.

Proposition 4.2 (Generalized second laws for arbitrary states)**.** *For any quantum states ρ, ρ', if the transition $\rho \to \rho'$ is possible with arbitrary accuracy, then*

i) For $\alpha \geq \frac{1}{2}$,

$$\hat{D}_\alpha(\rho||\tau^\beta) \geq \hat{D}_\alpha(\rho'||\tau^\beta), \tag{4.6.1}$$

ii) For $\frac{1}{2} \leq \alpha \leq 1$,

$$\hat{D}_\alpha(\tau^\beta||\rho) \geq \hat{D}_\alpha(\tau^\beta||\rho'), \tag{4.6.2}$$

iii) For $0 \leq \alpha \leq 2$,

$$\tilde{D}_\alpha(\rho||\tau^\beta) \geq \tilde{D}_\alpha(\rho||\tau^\beta). \tag{4.6.3}$$

This proposition follows directly from monotonicity under completely positive and trace-preserving maps, and additivity of the quantum Rényi divergences associated with the generalized free energies, as discussed in Section 2.3.1. More precisely, since catalytic thermal operations are CPTPMs, we have

$$\hat{D}_\alpha(\rho\ ||\tau^\beta) \geq \hat{D}_\alpha(\Lambda(\rho)||\Lambda(\tau^\beta)) = \hat{D}_\alpha(\rho'||\tau^\beta), \tag{4.6.4}$$

with the first inequality due to monotonicity of $\hat{D}_\alpha$ under CPTPMs Λ, and the second equality following from the fact that if $\Lambda(\rho) = \rho'$ is a CTO, then it preserves the thermal state.

These conditions are like second laws, in that they are necessary conditions which must be respected during a thermodynamic transition, however, they are not sufficient. This follows from the fact that there exists operations which are not catalytic thermal operations, but do preserve the thermal state, and they can transform a block-diagonal state to one which is not [104]. The above second laws would still hold according to data processing inequality. However, such a transition is impossible by CTOs.

4.7. CONCLUSIONS

The second law is often seen as arising from an experimenter's lack of control over the system of interest. Here we see that this is not the case: we obtain our fundamental limitations on state transition even in the case where the experimenter is allowed to access the microscopic degrees of freedom of the heat bath and couple it in an arbitrary manner with the system. The reason that such fine control does not lead to a violation of the second law is related to the fact that even a Maxwell's demon with microscopic control over a system cannot violate the second law, since a demon which knows the positions and momenta of the particles of a system, must record this information in a memory, which then needs to be reset at the end of a cyclic process [27, 84]. For the same reason, even if the experimenter is able to access the degrees of freedom of the heat bath, in order to violate the second law, he/she would also require work to reset his/her memory. Remarkably, it has recently been shown that although the limitations are derived assuming that one can perform all possible operations, it has been shown that they are also achievable using a more explicit set of operations, namely, changing the energy levels of the system, and putting parts of the system in thermal contact with the reservoir [105].

We have therefore derived a family of fundamental limitations on thermodynamical state transformations for both quasi-classical states, and fully quantum states. Since these limitations are given in terms of generalisations of the free energy, they can be thought of as second laws, combined with the first law, i.e. energy conservation. For an isolated system, one could take the second law to be the increase in the Rényi entropies, which holds if the allowed class of operations are mixtures of unitaries.

To summarize, in this chapter, we see that thinking of quantum thermodynamical interactions in a resource theoretic framework allows us to reformulate the laws of thermodynamics in a very natural way. In essence, the zeroeth law defines the set of allowed free states (the thermal state), the first law the set of allowed operations (namely, energy conser-

vation), and the second law is derived from these conditions to specify the set of allowed transitions. Furthermore, in [143], a statement about the amount of steps needed to cool to zero temperature has been derived, which is analogous to that of the third law.

5

INEXACT CATALYSIS

A complete picture of thermodynamical processes naturally allows for auxiliary systems dubbed "catalysts", i.e., any physical systems facilitating state transformations while staying close to intact in their original state, like an auxiliary system, a clock, or an actual catalyst. In this chapter, we present a comprehensive analysis of the power and limitation of such thermal catalysis. Specifically, we provide a family of optimal catalysts that can be returned with minimal trace distance error after facilitating a state transformation process. To incorporate the genuine physical role of a catalyst, we identify significant restrictions on arbitrary state transformations under dimension or mean energy bounds, using methods of convex relaxations. We discuss the implications of these findings on possible thermodynamic state transformations in the quantum regime.

5.1. INTRODUCTION

In Chapter 4, we have seen how the framework of thermal operations can be extended to catalytic thermal operations, by allowing the inclusion of a catalyst that undergoes a cyclic process. However, one needs to be precise about what one means by a cyclic process. At the macroscopic scale, the fact that a process is only approximately cyclic has generally been assumed to be enough to guarantee the second law. Here, we show that this is not the case in the microscopic regime, and we therefore need to quantify "how cyclic" a process is before stating the second law. Therefore, in this chapter, we explore what happens when one relaxes the conditions on how the catalyst should be returned.

Naturally, for physically realistic scenarios *inexact catalysis* is anticipated, where the catalyst is returned with a slight degradation. The loss of catalytic ability over time is often observed in chemical reactions, suggesting that catalysts often undergo slight changes in thermodynamic processes. In the quantum nano-regime, uncertainties such as those in the initial state, imperfections in implementation of quantum operations, or fluctuations induced by quantum noise can all serve to induce small changes in the catalyst. On physical grounds, it is unreasonable to suggest that the catalyst is returned in exactly the same way.

At the macroscopic scale, the fact that a process is only approximately cyclic has generally been assumed to be enough to guarantee the second law. However, we show that this is not the case anymore in the microscopic regime. Surprisingly, the conditions for catalytic transformations are highly non-robust against small errors induced in the catalyst, as we shall see later in this chapter. On physical grounds, such a setting seems implausible, and a clarification of this puzzle seems very much warranted.

A first hint towards a resolution may be provided by looking at how the error depends on the system size. The trace distance error ε depends on the dimension of the catalyst states $\dim(\omega_C) := n$; nevertheless one can find examples of catalysts where $\varepsilon \to 0$ as n approaches infinity. While examples show that in principle thermal embezzling may occur [125], hardly anything else is known otherwise. Indeed, it would be interesting to understand the crucial properties that distinguish between a catalyst and a non-thermal resource in thermodynamics. From a physical perspective, it seems highly desirable to understand to what the effect of embezzling can even occur for physically plausible systems.

5.1.1. RESULTS AND CONTRIBUTIONS

- We provide a quantitative statement about inexactly cyclic processes, by analyzing the case where the catalyst is returned only ε-close to its original state. We show that depending on the measure of closeness used to quantify how intact the catalyst is returned, different subsets of the generalized second laws would hold. This is shown in Section 5.2.

- We define the notion of *thermal embezzling*: instead of merely catalyzing the reaction, energy/purity has been extracted from the catalyst and used to facilitate thermodynamic transformations, while leaving the catalyst close to being intact [144].

- We investigate both the power and limitations of thermal embezzling. In the regime where both Hamiltonians of the system and catalyst are trivial, we perform an analytical construction of *universal* catalyst states, which are able to facilitate any state

transition on the system S (with some fixed dimension m). We show that for a catalyst to be universal, it is equivalent to facilitating a specific state transition, intuitively speaking the hardest possible transition on system S. By analysing such a problem, we then construct a family of *universal* catalyst states depending on catalyst dimension n, that achieves the optimal trace distance error. This is shown in Section 5.3.

- Given any general Hamiltonians of system and catalyst $\hat{H}_S, \hat{H}_C$, we identify two reasonable constraints of interest on the catalyst. Once either one of these constraints are satisfied, thermal embezzling cannot happen: 1) the dimension of the catalyst is bounded, and 2) when the expectation value of energy of the catalyst state is finite. For both cases, we derive non-zero bounds on the trace distance error, therefore showing that ε cannot be arbitrarily small. These bounds were derived under the assumption that the catalyst states are block-diagonal. Case 2) is especially interesting, since it holds for catalyst Hamiltonians with unbounded energy eigenvalues, as long as the partition function Z_C is finite. We then use these techniques to obtain more specific results: not only can we prevent thermal embezzling (which makes a statement about the ability of a catalyst to facilitate *any* state transition), but given any initial and final states ρ_S, σ_S, one can obtain *state-dependent* lower bounds on the trace distance error induced on the catalyst as well. This is shown in Section 5.4.

5.2. HOW TO QUANTIFY INEXACT CATALYSIS

In this section, we discuss three different measures of closeness between catalyst initial and final states:
1) the absolute trace distance,
2) the trace distance scaled by a factor depending on the dimension of the catalyst, and
3) a new quantity we define and refer to as the work distance.

5.2.1. THERMAL EMBEZZLING: TRIVIALIZATION OF ALL STATE TRANSITION CONDITIONS

At first glance, one might be tempted to demand that closeness should mean that ω_C is close to ω_C' in terms of the trace distance $d(\omega_C, \omega_C')$. After all, as discussed in Section 2.2.3, this quantity tells us how well one can distinguish two quantum states, given the best possible measurement strategy. In terms of the catalyst, one might hence ask that $d(\omega_C, \omega_C') \leq \varepsilon$ for some arbitrary small ε.

However, a phenomenon of embezzling is known in entanglement theory, which has important implications for the inclusion of such a catalyst. Embezzling states were originally introduced under the LOCC setting in Ref. [144]. An entangled state $|\nu(n)\rangle$ shared between parties A and B can be used to prepare some other state (of much smaller dimension),

$$|\nu(n)\rangle|0\rangle \longrightarrow |\omega\rangle \approx_\varepsilon |\nu(n)\rangle \otimes |\psi\rangle. \tag{5.2.1}$$

The fidelity of between the actual final state, $|\omega\rangle$, with $|\nu(n)\rangle \otimes |\psi\rangle$ is $1-\varepsilon$, such that ε goes to zero when n goes to infinity. This enables the approximate preparation of the state $|\psi\rangle$, while the embezzling resource state is also left close to its original state. Such a preparation can even be achieved simply via local operations (LO).

The family $|\nu(n)\rangle$ is therefore called a *universal embezzling state* if it enables the preparation of any $|\psi\rangle$ (of a fixed dimension). While this seemingly violates entanglement monotonicity under LOCC operations, one quickly realises that it is because the closeness in entanglement content of two states depend not only on the fidelity, but also the dimension. Hence although entanglement is exhausted, due to the large dimension, $|\nu(n)\rangle$ remains close to intact on the whole. In Ref. [145], a comprehensive study about general characteristics of embezzling states was conducted, providing insight into the necessary structure of a state to be a good embezzler. The power of embezzling in LOCC has been applied in several areas of quantum information, such as coherent state exchange protocols [146], projection games [147], or as a theoretical tool in proving the quantum reverse Shannon theorem [148].

There are some similarities between thermal embezzling and LOCC embezzling, however also many distinctive features exist. Most significantly, in thermodynamic systems, the Hamiltonian which determines the evolution of the system plays an important role in state conversion conditions [91]. This feature is absent in LOCC embezzling. We summarize the similarities and differences of LOCC and thermal embezzling in Table 5.1.

	LOCC embezzling	**Thermal embezzling**
State conversion conditions	Related to majorization/thermo-majorization	
Phenomena	The usage of a catalyst state of large dimension/energy while tolerating slight degradation allows the preparation of any desired target state to arbitrary precision	
Hamiltonians	Not of interest	Important physical significance
States (catalyst and system)	Pure, multipartite states	Mixed states in general
Commonly used measure of closeness	Fidelity of global state (system and embezzling state)	Trace distance between initial and final catalyst
Allowed operations	Catalytic LOCC LO operations	Catalytic thermal operations
Accuracy limited by	Dimension of catalyst	Dimension and energy

Table 5.1: An overview of differences between LOCC and thermal embezzling.

For noisy operations, where state transition conditions are described only by majorization, one may adapt the results of Ref. [144] to show that for any initial and final states ρ_S, ρ'_S, and any $\varepsilon > 0$, there exists a catalyst C with dimension n, such that using the catalyst state

$$\omega_C^1 = \frac{1}{Z(n)} \sum_{j=1}^{n} \frac{1}{j} |j\rangle\langle j| \,, \tag{5.2.2}$$

we may perform the transition $\rho_S \otimes \omega_C^1 \to \rho'_S \otimes \omega_C^1$ with trace distance error only ε. Here, $Z(n)$ is a normalisation constant. We shall see a more detailed analysis of thermal embezzling later in Section 5.3 and 5.4.

Another example of embezzling work can be adapted from an example in [144],

$$\omega_C^2 = |\psi\rangle\langle\psi| = \frac{1}{n}\sum_{j=1}^{n} |j\rangle\langle j|, \qquad \text{where } \hat{H}_C = \sum_{j=1}^{n} j|j\rangle\langle j|, \tag{5.2.3}$$

having that $\hat{H}_C$ is the Hamiltonian for a harmonic osciilator. If we consider an initial state $\rho_{SC} = |0\rangle\langle 0|_S \otimes |\psi\rangle\langle\psi|_C$, and apply the energy conserving operation

$$|0\rangle_S|j\rangle_C \to |1\rangle_S|j-1\rangle_C, \tag{5.2.4}$$

then by increasing n, ω_C^2 is left in a state $\frac{1}{n}$-close to its original state in trace distance, even though one unit of work (energy) has been transferred deterministically to the system.

Demanding that the catalyst be returned ε-close in trace distance is thus too weak a condition. Intuitively, the reason why it is too weak is that we may still need to consume a non-negligible amount of work to obtain the original catalyst from its returned version. If we therefore concieve of an approximately cylic process, as one which the working body is returned in a state which is ε-close in trace distance to its original form, then there is no second law. All state transformations are possible.

5.2.2. DIMINISHING TRACE DISTANCE: RECOVERY OF MACROSCOPIC SECOND LAW

We now consider the case where a catalyst is returned with accuracy $d(\omega_C, \omega_C') \leq \varepsilon/\ln N$, where N is the dimension of the catalyst. This means that not only the absolute value of trace distance error matters, but the error also has to decrease with the size of catalyst used. This is a further restriction compared to Section 5.2.1. We will see in such a case, we recover the usual second law that holds for macroscopic systems.

TRIVIAL HAMILTONIANS – RECOVERING THE SHANNON ENTROPY

Let us again first consider the case where $\hat{H}_S, \hat{H}_C$ are the trivial Hamiltonians. In particular, we will see that in the extensive regime only the Shannon entropy matters, and the Rényi entropies are no longer relevant. This shows that if we relax the conditions on how cyclic the process is, by allowing relatively large inaccuracies in the returned catalyst, then we recover the usual second law.

Theorem 5.1. *Consider any states $\rho, \rho' \in S(\mathcal{H}_S)$ where $\dim(S) = m$, and any $\varepsilon \in [0,1]$. Let $p = \mathrm{eig}(\rho)$ and $q = \mathrm{eig}(\rho')$ be the eigenvalues of the input and output state respectively. If there exists $N \in \mathbb{N}$ and a catalyst with spectrum $r \in V(N)$ such that*

$$p \otimes r \succ s, \qquad d(s, q \otimes r) \leq \frac{\varepsilon}{\ln N}, \tag{5.2.5}$$

then

$$H(p) \leq H(q) + \varepsilon + \frac{\varepsilon \ln m}{\ln N} + \mathrm{h}_2\left(\frac{\varepsilon}{\ln N}\right), \tag{5.2.6}$$

with $\mathrm{h}_2(x) := -x\ln(x) - (1-x)\ln(1-x)$ being the binary entropy.

Conversely, if

$$H(p) < H(q), \tag{5.2.7}$$

then for N sufficiently large there exists a catalyst with spectrum r of dimension N, and a final state s such that

$$p \otimes r \succ s, \qquad d(s, q \otimes r) \leq \exp\left(-\Theta\sqrt{\ln N}\right). \tag{5.2.8}$$

for some constant $c > 0$.

Proof. The forward direction is straightforward: suppose there exists a catalyst with spectrum r such that Eq. (5.2.5) holds true. Considering the bound on trace distance between s and $q \otimes r$, by Fannes inequality as presented in Theorem 2.1, we have

$$|H(s) - H(q \otimes r)| \leq \varepsilon + \frac{\varepsilon \ln m}{\ln N} + \mathrm{h}_2\left(\frac{\varepsilon}{\ln N}\right), \tag{5.2.9}$$

implying that

$$H(s) \leq H(q \otimes r) + \varepsilon + \frac{\varepsilon \ln m}{\ln N} + \mathrm{h}_2\left(\frac{\varepsilon}{\ln N}\right). \tag{5.2.10}$$

On the other hand, the majorization condition in Eq. (5.2.5) implies that

$$H(p \otimes r) \leq H(s) \leq H(q \otimes r) + \varepsilon + \frac{\varepsilon \ln m}{\ln N} + \mathrm{h}_2\left(\frac{\varepsilon}{\ln N}\right) \tag{5.2.11}$$

$$H(p) \leq H(q) + \varepsilon + \frac{\varepsilon \ln m}{\ln N} + \mathrm{h}_2\left(\frac{\varepsilon}{\ln N}\right). \tag{5.2.12}$$

Conversely, suppose Eq. (5.2.7) holds. Then we know that by typicality, and shown in Ref. [80], for all n sufficiently large, we have

$$p^{\otimes n} \succ \tilde{q}_n \tag{5.2.13}$$

for any $\tilde{q}_n$ such that for some constant $c > 0$,

$$d(\tilde{q}_n, q^{\otimes n}) \leq \exp(-c\sqrt{n}). \tag{5.2.14}$$

Let us consider the following catalyst introduced in [149]:

$$r = \frac{1}{n}\left[p^{\otimes(n-1)} \;\oplus\; q \otimes p^{\otimes(n-2)} \;\oplus\; \ldots \;\oplus\; q^{\otimes(n-2)} \otimes p \;\oplus\; q^{\otimes(n-1)}\right]. \tag{5.2.15}$$

We have

$$r \otimes p = \frac{1}{n}\left[p^{\otimes n} \;\oplus\; q \otimes p^{\otimes(n-1)} \;\oplus\; \ldots \;\oplus\; q^{\otimes(n-2)} \otimes p^{\otimes 2} \;\oplus\; q^{\otimes(n-1)} \otimes p\right]. \tag{5.2.16}$$

Now, let us consider the state

$$\hat{s} = \frac{1}{n}\left[\tilde{q}_n \;\oplus\; q \otimes p^{\otimes(n-1)} \;\oplus\; \ldots \;\oplus\; q^{\otimes(n-2)} \otimes p^{\otimes 2} \;\oplus\; q^{\otimes(n-1)} \otimes p\right]. \tag{5.2.17}$$

Upon observation, one may realize that the eigenvalues of this state $\hat{s}$ differs from $r \otimes p$ only by the first part, i.e. $p^{\otimes n}$ versus $\tilde{q}_n$. Since we already know that $p^{\otimes n} \succ \tilde{q}_n$, and since majorization is preserved under direct sum, it follows that

$$r \otimes p \succ \hat{s}. \tag{5.2.18}$$

Note that the eigenvalues of $r \otimes p$ and $p \otimes r$ are the same up to reordering. Now, let us consider the state

$$s = \frac{1}{n}\left[q \otimes p^{\otimes(n-1)} \;\oplus\; \ldots \;\oplus\; q^{\otimes(n-2)} \otimes p^{\otimes 2} \;\oplus\; q^{\otimes(n-1)} \otimes p \;\oplus\; \tilde{q}_n\right], \tag{5.2.19}$$

which is also simply the reordering of $\hat{s}$, by moving the eigenvalues of $\tilde{q}_n$ to the end. Since majorization only depends on eigenvalues, and not the order, we have that Eq. (5.2.18) also implies that $p \otimes r \succ s$.

Moreover, by writing out the state

$$q \otimes r = \frac{1}{n}\left[q \otimes p^{\otimes(n-1)} \;\oplus\; q^{\otimes 2} \otimes p^{\otimes(n-2)} \;\oplus\; \ldots \;\oplus\; q^{\otimes(n-1)} \otimes p \;\oplus\; q^{\otimes n}\right], \tag{5.2.20}$$

we see that the states $q \otimes r$ and s are extremely similar, except for the very last part. Therefore, we may calculate the trace distance, which is

$$d(s, q \otimes r) = \frac{1}{n} \cdot d(q_n, q^{\otimes n}) \leq \exp(-\Theta\sqrt{n}) = \exp\left(-\Theta\sqrt{\ln N}\right), \tag{5.2.21}$$

in the limit $n, N \to \infty$. The last equality holds because the dimension of r is $\dim(r) = N = n \cdot m^{n-1}$, and therefore in the limit $n \to \infty$, one has that $\ln N = \Theta(\ln n) + \ln m \cdot \Theta(n) = \Theta(n)$. □

GENERAL HAMILTONIANS – RECOVERING THE FREE ENERGY

Here we generalize the results of Theorem 5.1 for systems with a non-trivial Hamiltonian, only considering the case where ρ_S, ρ'_S are block-diagonal.

Theorem 5.2. *Consider $\varepsilon \geq 0$ and a system with some Hamiltonian $\hat{H}_S$ and $\dim(S) = m$, where the initial and final states ρ_S, ρ'_S are block-diagonal in the energy eigenbasis. If there exists a catalyst ω_C with spectrum of some dimension N (with some Hamiltonian $\hat{H}_C$) such that*

$$\rho_S \otimes \omega_C \xrightarrow[\text{TO}]{} \sigma_{SC}, \qquad d(\sigma_{SC}, \rho'_S \otimes \omega_C) \leq \frac{\varepsilon}{\max\left\{\ln N\,,\, E^{SC}_{\max}\right\}}, \tag{5.2.22}$$

where $E^S_{\max}$ is maximal energy of the Hamiltonian $\hat{H}_S$, then

$$F(\rho_S) \geq F(\rho'_S) - \varepsilon - \beta^{-1} \cdot \left[\varepsilon + \frac{\varepsilon \ln m}{\ln N} + \mathrm{h}_2\left(\frac{\varepsilon}{\ln N}\right)\right], \tag{5.2.23}$$

where $F(\rho) = \langle E \rangle - \beta^{-1} S(\rho)$ is the standard free energy.

Conversely, if

$$F(\rho_S) > F(\rho'_S), \tag{5.2.24}$$

then for all N sufficiently large, there exists a catalyst with spectrum of dimension N, and a final state σ_{SC} with a spectrum such that

$$\rho_S \otimes \omega_C \xrightarrow[\text{TO}]{} \sigma_{SC}, \qquad d(\sigma_{SC}, \rho'_S \otimes \omega_C) \leq \exp\left(-\Theta\left(\sqrt{\ln N}\right)\right). \tag{5.2.25}$$

Proof. The forward direction is again, relatively straightforward and similar to the proof found in Theorem 5.1, with the additional accounting for difference in average energy. Suppose there is a catalyst ω_C, and final state σ_{SC}, such that trace distance condition in Eq. (5.2.22) holds true. Then by Fannes inequality,

$$\left|S(\sigma_{SC}) - S(\rho'_S \otimes \omega_C)\right| \leq \varepsilon + \frac{\varepsilon \ln d}{\ln N} + \mathrm{h}_2\left(\frac{\varepsilon}{\ln N}\right). \tag{5.2.26}$$

Also, we have that

$$\left|\langle E\rangle_{\sigma_{SC}} - \langle E\rangle_{\rho'_S \otimes \omega_C}\right| \leq d(\sigma_{SC}, \rho'_S \otimes \omega_C) \cdot E_{\max}^{SC} \leq \varepsilon. \tag{5.2.27}$$

Therefore,

$$\begin{aligned} \left|F(\sigma_{SC}) - F(\rho'_S \otimes \omega_C)\right| &\leq \left|\langle E\rangle_{\rho} - \langle E\rangle_{\rho'}\right| + \beta^{-1}\left|S(\sigma_{SC}) - S(\rho'_S \otimes \omega_C)\right| && (5.2.28)\\ &\leq \varepsilon + \beta^{-1}\left[\varepsilon + \frac{\varepsilon \ln d}{\ln N} + \mathrm{h}_2\left(\frac{\varepsilon}{\ln N}\right)\right], && (5.2.29) \end{aligned}$$

which implies that

$$F(\sigma_{SC}) \geq F(\rho'_S \otimes \omega_C) - \varepsilon - \beta^{-1} \cdot \left[\varepsilon + \frac{\varepsilon \ln d}{\ln N} + \mathrm{h}_2\left(\frac{\varepsilon}{\ln N}\right)\right]. \tag{5.2.30}$$

Furthermore, we know that since $\rho_S \otimes \omega_C \xrightarrow[\mathrm{TO}]{} \sigma_{SC}$,

$$F(\rho_S \otimes \omega_C) \geq F(\sigma_{SC}). \tag{5.2.31}$$

Eqns. (5.2.30) and (5.2.31) jointly give Eq. (5.2.23), while noting that the free energy is additive under tensor product, i.e. $F(\rho_1 \otimes \rho_2) = F(\rho_1) + F(\rho_2)$.

Conversely, suppose that Eq. (5.2.24) holds. Then from the main result of Ref. [80] we know that for n sufficiently large,

$$\rho_S^{\otimes n} \xrightarrow[\mathrm{TO}]{} \tilde{\rho}, \tag{5.2.32}$$

with

$$d(\tilde{\rho}, \rho_S'^{\otimes n}) \leq \exp\left(-\Theta\sqrt{n}\right). \tag{5.2.33}$$

Furthermore, since for block-diagonal states, the conditions for state transition are solely governed by thermo-majorization, we only need to concern ourselves with the ordered eigenvalues of involved states. We will therefore continue the discussion by identifying the states directly with its corresponding eigenvalue spectrum: let $p = \mathrm{eig}(\rho_S)$, $q = \mathrm{eig}(\rho'_S)$ and $q_n = \mathrm{eig}(\tilde{\rho})$. Let us, then, given the Hamiltonian $\hat{H}_S$, consider a catalyst with the following (much larger) Hamiltonian:

$$\hat{H}_C = \bigoplus_{k=1}^{n} \sum_{i=1}^{n-1} \hat{H}_S^{(i)}, \tag{5.2.34}$$

where $\hat{H}_S^{(i)} = \overbrace{\mathbb{1}\ldots\otimes\underbrace{\hat{H}_S}_{i\text{-th site}}\otimes\mathbb{1}\otimes\ldots\otimes\mathbb{1}}^{n-1\text{ terms}}$. Furthermore, let us take the state of catalyst, ω_C, to have a spectrum r of the form in Eq. (5.2.15), which we write out again for convenience:

$$r = \frac{1}{n}\left[p^{\otimes(n-1)} \oplus q\otimes p^{\otimes(n-2)} \oplus \ldots \oplus q^{\otimes(n-2)}\otimes p \oplus q^{\otimes(n-1)}\right]. \tag{5.2.35}$$

Let us also write out the spectrum of $\omega_C\otimes\rho_S$ and $\rho_S'\otimes\omega_C$:

$$r\otimes p = \frac{1}{n}\left[p^{\otimes n} \oplus q\otimes p^{\otimes(n-1)} \oplus \ldots \oplus q^{\otimes(n-2)}\otimes p^{\otimes 2} \oplus q^{\otimes(n-1)}\otimes p\right], \tag{5.2.36}$$

$$q\otimes r = \frac{1}{n}\left[q\otimes p^{\otimes(n-1)} \oplus q^{\otimes 2}\otimes p^{\otimes(n-2)} \oplus \ldots \oplus q^{\otimes(n-1)}\otimes p \oplus q^{\otimes n}\right]. \tag{5.2.37}$$

Upon observation, one may define the vector $\tilde{r}$, such that Eqns. (5.2.36), (5.2.37) can be rewritten as

$$\mathrm{eig}(\omega_C\otimes\rho_S) = r\otimes p = \frac{1}{n}p^{\otimes n}\oplus\tilde{r}, \qquad \mathrm{eig}(\rho_S'\otimes\omega_C) = q\otimes r = \tilde{r}\oplus\frac{1}{n}q^{\otimes n}, \tag{5.2.38}$$

where $\tilde{r} := \frac{1}{n}\left[q\otimes p^{\otimes(n-1)} \oplus q^{\otimes 2}\otimes p^{\otimes(n-2)} \oplus \ldots \oplus q^{\otimes(n-1)}\otimes p\right]$.

Now, let us finally note that if we consider the block-diagonal states $\rho_{\mathrm{in}}, \rho_{\mathrm{out}}$ such that $\mathrm{eig}(\rho_{\mathrm{in}}) = \frac{1}{n}p^{\otimes n}\oplus\tilde{r}$, and that $\mathrm{eig}(\rho_{\mathrm{out}}) = \tilde{r}\oplus\frac{1}{n}q_n$, then there exists a thermal operation $\mathcal{N}$ that performs the following transition:

$$\rho_{\mathrm{in}} \xrightarrow[\mathrm{TO}]{} \rho_{\mathrm{out}}. \tag{5.2.39}$$

Indeed, one may first apply a thermal operation that transforms the eigenvalues $p^{\otimes n}$ into q_n, which was shown to exist in Ref. [80], as we have mentioned above in Eq. (5.2.32). Subsequently, since for each block under the direct sum of Eq (5.2.34), the Hamiltonian is identical, one may switch the eigenvalues of the spectrum from the first term of the direct sum, to the levels of its last term. This can be done because the energy levels of the Hamiltonian are the same across the direct sum (note the form of $\hat{H}_C$).

So far, we have a thermal operation $\mathcal{N}$ that brings the initial state (corresponding to spectra $r\otimes p$) to a final state close to the target (corresponding to spectra $q\otimes r$). Then we reverse the above switching operation. Now, the result follows by

$$d(\rho_{\mathrm{out}}, \rho_S'\otimes\omega_C) = d(\tilde{r}\oplus\frac{1}{n}q_n, \tilde{r}\oplus\frac{1}{n}q^{\otimes n}) \leq \frac{1}{n}\cdot d(q_n, q^{\otimes n}) = \exp\left(-\Theta\left(\sqrt{\ln N}\right)\right) \tag{5.2.40}$$

and the last inequality comes from applying Eq. (5.2.33) and the fact that the dimension of the catalyst is $N = n\cdot m^{n-1}$. □

5.2.3. WORK DISTANCE: AN OPERATIONAL CLOSENESS MEASURE BETWEEN STATES

The last closeness measure we consider, takes an operational perspective on the problem of inexact catalysis. More precisely, we propose to require that the catalyst should be returned

in a form such that, only a small amount of work is needed in order restore (via exact catalysis) the catalyst to its original form. This is natural, in the sense that if someone loans you a catalyst, then they would want it returned in such a way that it does not require a large amount of work to restore it back.

We thus consider the inexact transition

$$\rho_S^0 \otimes \rho_C^0 \to \rho_{SC}^1, \tag{5.2.41}$$

and require that ρ_C^1 should be such that the restoration $\rho_C^1 \xrightarrow[\text{CTO}]{} \rho_C^0$ should only require an ε amount of work. This prompts our definition of the work distance below.

Definition 5.1. *Consider states ρ, ρ' corresponding to some Hamiltonian $\hat{H}$. Furthermore, consider a qubit battery that has Hamiltonian $\hat{H}_W = W|W\rangle\langle W|$. The work distance from ρ to ρ' is given by*

$$D_{\text{work}}(\rho \succ \rho') := \inf \{W \in \mathbb{R} \mid \rho \otimes |W\rangle\langle W|_W \xrightarrow[\text{CTO}]{} \rho' \otimes |0\rangle\langle 0|_W\}. \tag{5.2.42}$$

Since in Chapter 4, we have shown necessary and sufficient conditions for a state transition via CTOs, we may apply these laws to evaluate $D_{\text{work}}(\rho \succ \rho')$ in the case where ρ, ρ' are block-diagonal. More concretely, we know that $\rho \otimes |W\rangle\langle W|_W \xrightarrow{\text{CTO}} \rho' \otimes |0\rangle\langle 0|_W$ is possible iff for $\forall \alpha \geq 0$,

$$F_\alpha(\rho \| \tau^\beta) + \frac{\beta^{-1}}{\alpha - 1} \ln \left[\frac{e^{-\beta W}}{1 + \mathrm{e}^{-\beta W}} \right]^{1-\alpha} \geq F_\alpha(\rho_S^1 \| \tau_S^\beta) + \frac{\beta^{-1}}{\alpha - 1} \ln \left[\frac{1}{1 + \mathrm{e}^{-\beta W}} \right]^{1-\alpha}, \tag{5.2.43}$$

where rearranging yields

$$F_\alpha(\rho \| \tau^\beta) + W \geq F_\alpha(\rho' \| \tau^\beta)\ , \tag{5.2.44}$$

and therefore

$$W \geq F_\alpha(\rho' \| \tau^\beta) - F_\alpha(\rho \| \tau^\beta) = \beta^{-1} \cdot \left[D_\alpha(\rho' \| \tau^\beta) - D_\alpha(\rho \| \tau^\beta) \right]. \tag{5.2.45}$$

This implies that for block-diagonal states ρ, ρ', the work distance is given by

$$D_{\text{work}}(\rho \succ \rho') = \beta^{-1} \sup_{\alpha \geq 0} \left[D_\alpha(\rho' \| \tau^\beta) - D_\alpha(\rho \| \tau^\beta) \right]. \tag{5.2.46}$$

In Ref. [91], the extractable work from a state (by thermalizing it) and the work cost for its formation (starting with a thermal state) via thermal operations have been given by

$$\hat{W}_{\text{ext}}(\rho) = -\beta^{-1} \ln \operatorname{tr}(\Pi_\rho \tau_\beta) = \beta^{-1} \tilde{D}_0(\rho \| \tau^\beta) \tag{5.2.47}$$

$$\hat{W}_{\text{cost}}(\rho) = \beta^{-1} \ln \min\{\lambda : \rho \leq \lambda \tau_\beta\} = \beta^{-1} \tilde{D}_\infty(\rho \| \tau^\beta), \tag{5.2.48}$$

These conditions arise as special cases of our conditions, as we see in the subsequent corollary: the work distance reduces to these quantities.

Corollary 5.1. *Consider a block-diagonal state ρ. Then the following holds:*

- *The maximum extractable work* $\hat{W}_{\text{ext}}(\rho) = -\mathrm{D}_{\text{work}}(\rho \succ \tau^\beta)$.
- *The minimum work cost* $\hat{W}_{\text{cost}}(\rho) = \mathrm{D}_{\text{work}}(\tau^\beta \succ \rho)$.

Proof. To evaluate $\mathrm{D}_{\text{work}}(\rho \succ \tau)$, note that $\forall \alpha$, $D_\alpha(\tau^\beta \| \tau^\beta) = 0$. On the other hand, since ρ is block-diagonal, it commutes with τ^β, and hence $\tilde{D}_\alpha(\rho \| \tau^\beta) = D_\alpha(\rho \| \tau^\beta)$. Therefore,

$$-\mathrm{D}_{\text{work}}(\rho \succ \tau^\beta) = -\beta^{-1} \cdot \sup_{\alpha>0} \left[-D_\alpha(\rho \| \rho^\beta)\right] = \beta^{-1} \cdot \inf_{\alpha>0} \left[D_\alpha(\rho \| \tau^\beta)\right] = \hat{W}_{\text{ext}}(\rho),$$

where the last equality holds due to the fact that the Rényi divergences are non-decreasing in positive α. On the other hand,

$$\mathrm{D}_{\text{work}}(\tau^\beta \succ \rho) = \beta^{-1} \cdot \sup_{\alpha>0} D_\alpha(\rho \| \tau^\beta) = \hat{W}_{\text{cost}}(\rho).$$

□

Let us now return to the discussion of catalysis, where we demand that the catalyst is returned, such that the work distance for resetting the catalyst to its original state is small, i.e. $D_{\text{work}}(\rho_C^1 \succ \rho_C^0) \leq \varepsilon$. In the case where inexact catalysis occurs, we are allowed to borrow a catalyst ρ_C^0 and conduct the transformation $\rho_S^0 \otimes \rho_C^0 \to \rho_{SC}^1$. If this transformation is allowed via thermal operations, then we know for all $\alpha \geq 0$,

$$F_\alpha(\rho_S^0 \otimes \rho_C^0, \rho_S^\beta \otimes \rho_C^\beta) \geq F_\alpha(\rho_{SC}^1, \rho_S^\beta \otimes \rho_C^\beta). \tag{5.2.49}$$

If $\rho_{SC}^1 = \rho_S^1 \otimes \rho_C^1$ is of product form[1], and if the cost of restoring the catalyst has to be small, $\mathrm{D}(\rho_C^1 \succ \rho_C^0) \leq \varepsilon$, then

$$\begin{aligned}
F_\alpha(\rho_S^0 \otimes \rho_C^0, \rho_S^\beta \otimes \rho_C^\beta) &\geq F_\alpha(\rho_S^1, \rho_S^\beta) + F_\alpha(\rho_S^1, \rho_C^\beta) && (5.2.50)\\
F_\alpha(\rho_S^0, \rho_S^\beta) &\geq F_\alpha(\rho_S^1, \rho_S^\beta) + F_\alpha(\rho_C^1, \rho_C^\beta) - F_\alpha(\rho_C^0, \rho_C^\beta) && (5.2.51)\\
&\geq F_\alpha(\rho_S^1, \rho_S^\beta) + \inf_{\alpha>0} \left[F_\alpha(\rho_C^1, \rho_C^\beta) - F_\alpha(\rho_C^0, \rho_C^\beta)\right] && (5.2.52)\\
&\geq F_\alpha(\rho_S^1, \rho_S^\beta) - \sup_{\alpha>0} \left[F_\alpha(\rho_C^0, \rho_C^\beta) - F_\alpha(\rho_C^1, \rho_C^\beta)\right] && (5.2.53)\\
&\geq F_\alpha(\rho_S^1, \rho_S^\beta) - \varepsilon, && (5.2.54)
\end{aligned}$$

which tells us that all our second laws are (approximately) recovered.

5.3. THE POWER OF THERMAL EMBEZZLING

In this section, we explore in detail the phenomena of thermal embezzling, which we encountered in Section 5.2.1. We saw that the trace distance, although enjoying an operational significance in quantum information and commonly regarded as the standard tool to quantify distance between quantum states, when applied to inexact catalysis in thermodynamics, neglects information about the dimension/energy of the catalyst. Therefore, if trace distance

[1] For non-product output distributions, this argument does not hold since the α free energies are not superadditive, namely $F_\alpha(\rho_{AB}, \sigma_{AB}) \geq F_\alpha(\rho_A, \sigma_A) + F_\alpha(\rho_B, \sigma_B)$ is generally not true.

is to be used for the quantification of catalytic error, then further conditions should be stated on the Hamiltonian/dimension of the catalyst as well.

To formulate such conditions, let us first explore the power of thermal embezzling. To do so, we consider the scenario of preparing a pure excited state of maximum energy[2]

$$\Pi^S_{\max} = |E^S_{\max}\rangle\langle E^S_{\max}| \tag{5.3.1}$$

from a thermal state τ^β_S, where β is the inverse temperature of the reservoir used in thermal operations. Intuitively, if we are interested only in block-diagonal state transitions, then this is the hardest thermal embezzling scenario possible. This is because for any block-diagonal ρ_S, the state $\Pi^S_{\max}$ thermo-majorizes ρ_S, which in turn thermo-majorizes τ^β_S. Therefore, it suffices to analyze the preparation of such a pure excited state,

$$\omega_C \otimes \tau^\beta_S \xrightarrow[\text{TO}]{} \omega'_C \otimes \Pi^S_{\max}, \tag{5.3.2}$$

which is possible iff $\omega_C \otimes \tau^\beta_S$ thermo-majorizes $\omega'_C \otimes \Pi^S_{\max}$. In the next lemma, we make precise this argument, by showing that given fixed Hamiltonians, any catalyst state that succeeds in preparing such a state can also be used to facilitate any other state transformation.

Lemma 5.1 (Universal embezzlers for block-diagonal states)**.** *Suppose there exists block-diagonal catalysts ω_C, ω'_C (with Hamiltonian $\hat{H}_C$) such that $\omega_C \otimes \tau^\beta_S \xrightarrow[\text{TO}]{} \omega'_C \otimes \Pi^S_{\max}$ holds. Then for any states ρ_S, ρ'_S diagonal (in $\hat{H}_S$), $\omega_C \otimes \rho_S \xrightarrow[\text{TO}]{} \omega'_C \otimes \rho'_S$ holds as well.*

Proof. This can be proven by noting that having $\omega_C \otimes \tau^\beta_S$ thermo-majorizes $\omega'_C \otimes \Pi^S_{\max}$, is equivalent to the existence a β-thermal operation denoted by $\mathcal{M}$, such that $\mathcal{M}(\omega_C \otimes \tau^\beta_S) = \omega'_C \otimes \Pi^S_{\max}$. It remains to show that for any ρ_S, ρ'_S, there exists a thermal operation $\mathcal{M}'$ such that $\mathcal{M}'(\omega_C \otimes \rho_S) = \omega'_C \otimes \rho'_S$. Since the thermal state τ^β_S is thermo-majorized by any state ρ_S, and $\Pi^S_{\max}$ thermo-majorizes any other state ρ'_S, there exist thermal operations $\mathcal{N}_1, \mathcal{N}_2$ such that $\mathcal{N}_1(\rho_S) = \tau^\beta_S$ and $\mathcal{N}_2(\Pi_{\max}) = \rho'_S$. Finally, consider

$$\mathcal{M}' = (\mathbb{1}_C \otimes \mathcal{N}_2) \circ \mathcal{M} \circ (\mathbb{1}_C \otimes \mathcal{N}_1), \tag{5.3.3}$$

then $\mathcal{M}'(\omega_C \otimes \rho_S) = \omega'_C \otimes \rho'_S$. This implies $\omega_C \otimes \rho_S$ thermo-majorizes $\omega'_C \otimes \rho'_S$. □

We begin by exploring the case for trivial Hamiltonians, where it is known that thermal embezzling can occur. Recall that in this regime, thermal states are simply maximally mixed states, and all unitary operations are allowed. In such cases, the thermo-majorization condition reduces to majorization: $\rho \xrightarrow[\text{NO}]{} \rho'$ is possible iff $\rho \succ \rho'$. To investigate thermal embezzling in this setting, one asks if given fixed dimensions $\dim(S) = m$ and $\dim(C) = n$, what is the smallest ε such that there exists a catalyst state ω_C that satisfies

$$\omega_C \otimes \frac{\mathbb{1}_S}{m} \succ \omega'_C \otimes |0\rangle\langle 0|_S, \tag{5.3.4}$$

[2] In the case where the maximum energy is degenerate, any pure state within the degenerate subspace suffices.

where the trace distance $d(\omega_C, \omega'_C)$ between the initial catalyst ω_C and final catalyst ω'_C is not greater than ε. This trace distance is used as a measure of catalytic error throughout our analysis. If some catalyst pair (ω_C, ω'_C) satisfies condition Eq. (5.3.4) with trace distance ε, then it also facilitates $\omega_C \otimes \rho_S \xrightarrow[\text{NO}]{} \omega'_C \otimes \rho'_S$ for any m-dimensional states ρ, ρ'[3].

Definition 5.2. *Consider systems S, C such that $\dim(S) = m \geq 2$ and $\dim(C) = n = m^a$ where $a \geq 1$. Let $\mathscr{S}_{m,n}$ be the set of n-dimensional catalyst state pairs (ω_C, ω'_C) enabling the transformation $\omega_C \otimes \frac{1}{m}\mathbb{1}_S \xrightarrow[\text{NO}]{} \omega'_C \otimes |0\rangle\langle 0|_S$, by satisfying*

$$\omega_C \otimes \frac{1}{m}\mathbb{1}_S \succ \omega'_C \otimes |0\rangle\langle 0|_S. \tag{5.3.5}$$

Let $d_{m,n} = \min\left\{d\left(\omega_C, \omega'_C\right) \mid \left(\omega_C, \omega'_C\right) \in \mathscr{S}_{m,n}\right\}$.

Since majorization conditions depend solely on the eigenvalues of the density matrices ω_C and ω'_C, one can phrase this solution for $d_{m,n}$ in terms of a linear minimization program over catalyst states diagonal and ordered in the same basis. In fact, the eigenvalues of ω_C, ω'_C which give rise to optimal trace distance error can be solved by such a linear program, although for general values of n and m, these eigenvalues are non-unique, and it is harder to construct an analytical solution. Whenever $m \geq 2$ and $n = m^a$ where $a \geq 1$ is an integer, we provide an analytic construction of catalyst states, which we later show to be optimal for the state transformation in Eq. (5.3.4).

5.3.1. A FAMILY OF CATALYST STATES

Lemma 5.2. *Consider a system S such that $\dim(S) = m$, and a catalyst C such that $\dim(C) = n = m^a$ for some integer $a \geq 1$. Consider the following catalyst state pair (ω_C, ω'_C): the state $\omega'_C = \sum_{i=1}^{n} \omega'_i |i\rangle\langle i|$, where*

$$\omega'_1 = \frac{1}{1 + (m-1)a} \text{ and } \omega'_i = \omega'_1 m^{1-\lceil \log_m i \rceil}. \tag{5.3.6}$$

On the other hand, $\omega_C = \sum_{i=1}^{n} \omega_i |i\rangle\langle i|$, where

$$\omega_i = \begin{cases} \omega'_1 \cdot m & \text{if } i = 1, \\ \omega'_i & \text{if } 2 \leq i \leq \frac{n}{m}, \\ 0 & \text{if } i > \frac{n}{m}. \end{cases} \tag{5.3.7}$$

Then the pair $(\omega_C, \omega'_C) \in \mathscr{S}_{m,n}$ as defined in Def. 5.2, and therefore

$$d_{m,n} \leq d(\omega_C, \omega'_C) = \frac{m-1}{1 + (m-1)a}. \tag{5.3.8}$$

Proof. Before we begin the proof, it might be helpful to gain some intuition of what the structure of ω_C, ω'_C looks like. For ω'_C, a simple way to visualise this is as follows: for the

[3] This follows from Lemma 5.1 and substituting $\hat{H}_S = \mathbf{0}$.

first m elements, the distribution is uniform with some probability ω_1; for the next $m+1$ up to m^2 elements the distribution is uniform again, with probability ω_1/m; and so on up to $n = m^a$. The initial ω_1 is then chosen so that the full distribution is normalised. As for ω_C, such a state is obtained from ω'_C by setting all the probabilities for $i > n/m$ to be zero, while renormalizing by increasing the largest peak of the probability distribution.

Here, we prove that $\omega_C \otimes \frac{1}{m}\mathbb{1}_S \succ \omega'_C \otimes |0\rangle\langle 0|_S$, the majorization relation as stated in Def. 5.2. It is very easy to see that this is true, once the eigenvalues of ω_C and ω'_C are compared

$$\omega'_C = \mathrm{diag}\Bigg(\underbrace{\omega'_1, \cdots\cdots\cdots, \omega'_1}_{m},\ \underbrace{\frac{\omega'_1}{m}, \cdots, \frac{\omega'_1}{m}}_{m(m-1)},\ \underbrace{\frac{\omega'_1}{m^2}, \cdots, \frac{\omega'_1}{m^2}}_{m(m^2-m)},\ \cdots\cdots,\ \underbrace{\frac{\omega'_1}{m^{a-2}}, \cdots, \frac{\omega'_1}{m^{a-2}}}_{m(m^{a-2}-m^{a-3})}, \underbrace{\frac{\omega'_1}{m^{a-1}}, \cdots, \frac{\omega'_1}{m^{a-1}}}_{m(m^{a-1}-m^{a-2})}\Bigg) \tag{5.3.9}$$

$$\omega_C = \mathrm{diag}\Bigg(m\omega'_1, \underbrace{\omega'_1, \cdots, \omega'_1}_{m-1},\ \underbrace{\frac{\omega'_1}{m}, \cdots, \frac{\omega'_1}{m}}_{m^2-m},\ \underbrace{\frac{\omega'_1}{m^2}, \cdots, \frac{\omega'_1}{m^2}}_{m^3-m^2},\ \cdots\cdots,\ \underbrace{\frac{\omega'_1}{m^{a-2}}, \cdots, \frac{\omega'_1}{m^{a-2}}}_{m^{a-1}-m^{a-2}},\ \underbrace{0, \cdots\cdots\cdots\cdots, 0}_{m^a-m^{a-1}}\Bigg), \tag{5.3.10}$$

where we have written this by making use of the fact that $m^k - m^{k-1} = m(m^{k-1} - m^{k-2})$.

Firstly, one can observe that since $|0\rangle\langle 0|_S$ is a pure state with a single eigenvalue 1, therefore $\omega'_C \otimes |0\rangle\langle 0|$ has the same eigenvalues as ω'_C. On the other hand, for any two eigenvalues in ω_C, if one is greater than the other, then it is greater by at least a factor of m. This implies that when we consider $\omega_C \otimes \frac{1}{m}\mathbb{1}_S$, the order of these eigenvalues will not change. One can obtain the eigenvalues of $\omega_C \otimes \frac{1}{m}\mathbb{1}_S$ simply by dividing *each* eigenvalue of ω_C by a factor m, while increasing its multiplicity also by a factor of m. However, by doing so using Eq. (5.3.10), one sees that we obtain a set of eigenvalues *exactly equal* to those in Eq. (5.3.9). Since any vector majorizes itself, we conclude that $\omega_C \otimes \frac{\mathbb{1}_S}{m} \succ \omega'_C \otimes |0\rangle\langle 0|_S$.

In calculating the trace distance between ω_C and ω'_C, note firstly that ω_C, ω'_C are diagonal in the same basis, therefore we need only consider the eigenvalues. Furthermore, $\omega_1 > \omega'_1$ while $\omega_i \leq \omega'_i$ for all $i > 2$. Therefore,

$$d(\omega_C, \omega'_C) = \frac{1}{2}\sum_{i=1}^{n} |\omega_i - \omega'_i| = \sum_{i:\omega_i > \omega'_i} (\omega_i - \omega'_i) = \omega_1 - \omega'_1 = \frac{m-1}{1+(m-1)a}. \tag{5.3.11}$$

This shows that

$$d_{m,n} \leq \frac{m-1}{1+(m-1)a}, \tag{5.3.12}$$

since we have constructed a specific state pair achieving this trace distance. This bound shows that $d_{m,n}$ decreases with $a = \log_m n$. □

In the next section we will see that for catalysts satisfying Eq. (5.3.5), smaller values of trace distance cannot be achieved, which implies that Eq. (5.3.12) is true with equality, and the family presented in Lemma 5.2 is optimal.

5.3.2. OPTIMAL CATALYSIS

In this section we show by induction that

$$d_{m,n} \geq \frac{m-1}{1+(m-1)a}. \tag{5.3.13}$$

Recall that our problem is to minimize the trace distance $d(\omega_C, \omega'_C)$ over states ω_C, ω'_C such that Eq. (5.3.5) is satisfied. We first show that it suffices to minimize over states which are diagonal in the same basis.

Lemma 5.3 (Optimal initial and final catalyst pairs are diagonal in the same basis)**.** *Consider fixed n-tuples of eigenvalues* $(\omega_1, \cdots, \omega_n)$ *and* $(\omega'_1, \cdots, \omega'_n)$*, such that* $\omega_C = \sum_i \omega_i |e_i\rangle\langle e_i|$ *and* $\omega'_C = \sum_i \omega'_i |f_i\rangle\langle f_i|$ *are diagonal in two different bases* $\{|e_i\rangle\}, \{|f_i\rangle\}$*. If* (ω_C, ω'_C) *satisfies Eq.* (5.3.5)*, then there exists* $\tilde{\omega}_C = \sum_i \tilde{\omega}_i |e_i\rangle\langle e_i|$ *such that* $d(\omega_C, \omega'_C) \geq d(\omega_C, \tilde{\omega}_C)$ *and that* $(\omega_C, \tilde{\omega}_C)$ *also satisfies Eq.* (5.3.5)*.*

Proof. There are two steps in this proof: firstly, we construct $\tilde{\omega}_C$ from ω'_C and show that the trace distance decreases by invoking data processing inequality. Then, we use Schur's theorem to show that majorization holds.

Let $\tilde{\omega}_C = \mathcal{N}(\omega'_C)$, where $\mathcal{N}(\rho) = \sum_i |e_i\rangle\langle e_i|\rho|e_i\rangle\langle e_i|$ is the fully dephasing channel in the basis $\{|e_i\rangle\}$. Note that since ω_C is already diagonal in $\{|e_i\rangle\}$, $\mathcal{N}(\omega_C) = \omega_C$. Because the trace distance is non-increasing under CPTPMs, in particular TOs, we have

$$d(\omega_C, \omega'_C) \geq d(\mathcal{N}(\omega_C), \mathcal{N}(\omega'_C)) = d(\omega_C, \tilde{\omega}_C)\ . \tag{5.3.14}$$

On the other hand, we will show that $\omega'_C \succ \tilde{\omega}_C$; in other words, $\mathrm{eig}(\omega'_C) \succ \mathrm{eig}(\tilde{\omega}_C)$. Recall that $\tilde{\omega}_C = \mathcal{N}(\omega'_C)$ and, from the definition of $\mathcal{N}$, observe that the eigenvalues $\mathrm{eig}(\tilde{\omega}_C)$ are precisely the diagonal elements of ω'_C in the basis $\{|e_i\rangle\}$. Schur's theorem (which we've seen in Theorem 2.4) says that for any Hermitian matrix M, $\mathrm{eig}(M)$ majorizes the diagonal elements of M. Therefore, we have that $\omega'_C \succ \tilde{\omega}_C$. Making use of the initial assumption $\omega_C \otimes \mathbb{I}_S/m \succ \omega'_C \otimes |0\rangle\langle 0|_S$, we now see that

$$\omega_C \otimes \frac{1}{m}\mathbb{I}_S \succ \omega'_C \otimes |0\rangle\langle 0|_S \succ \tilde{\omega}_C \otimes |0\rangle\langle 0|_S\ , \tag{5.3.15}$$

which concludes the proof. □

We are now ready to establish a lower bound on $d_{m,n}$ for $n = m^a$, where we use Lemma 5.3 so that we only consider cases where both states are simultaneously diagonalized.

Theorem 5.3. *Consider integers* $m \geq 2$ *and* $n = m^a$ *where* $a \geq 1$*. Then*

$$d_{m,n} = \frac{m-1}{1+(m-1)a}, \tag{5.3.16}$$

where $d_{m,n}$ is defined in Def. (5.2). Hence, the family of catalyst states from Section 5.3.1 achieves this optimal trace distance.

Proof. To begin, note that the majorization condition

$$\omega_C \otimes \frac{1}{m}\mathbb{I}_S \succ \omega'_C \otimes |0\rangle\langle 0|_S \tag{5.3.17}$$

only depends on the eigenvalues of ω and ω'. For fixed eigenvalues, the trace distance $d(\omega,\omega')$ is minimized if the two states share the same eigenbasis and the eigenvalues are ordered in the same way, *e.g.*, in decreasing order, as discussed in Lemma 5.3. Hence, from now on we consider only diagonal states $\omega = \mathrm{diag}(\omega_1,\ldots,\omega_n)$ and $\omega' = \mathrm{diag}(\omega'_1,\ldots,\omega'_n)$, where $\omega_1 \geq \omega_2 \geq \ldots \geq \omega_n$ and $\omega'_1 \geq \omega'_2 \geq \ldots \geq \omega'_n$. Here, $\mathrm{diag}(\cdots)$ denotes the diagonal matrix with the corresponding diagonal elements. To prove the theorem, we only need to show that

$$d_{m,n} \geq \frac{m-1}{1+(m-1)a} \tag{5.3.18}$$

as the other inequality follows from the family of embezzling states exhibited in Lemma 5.2. We use induction on the integer a. For the base case $a = 1$, we need to show that $d_{m,m} \geq 1 - 1/m$. Consider any feasible solution (ω,ω') in dimension $n = m$. From the majorization condition

$$\omega \otimes \frac{1}{m}\mathbb{I}_m \succ \omega' \otimes |0\rangle\langle 0| \;\Leftrightarrow\; \left(\frac{\omega_1}{m},\ldots,\frac{\omega_1}{m},\ldots,\frac{\omega_m}{m},\ldots,\frac{\omega_m}{m}\right) \succ (\omega'_1,\ldots,\omega'_m,0,\ldots,0) \tag{5.3.19}$$

it follows that $\omega_1/m \geq \omega'_1$ and $\omega_i = 0$ for $i \geq 2$. Hence, $\omega_1 = 1$ and $1/m \geq \omega'_1$. Since ω'_1 is the largest of the m values ω'_i, we get $\omega'_i = 1/m$ for all i. Finally, a simple calculation reveals that $d(\omega,\omega') = 1 - 1/m$, which establishes the base case.

For the inductive step, we assume that

$$d_{m,n} = \frac{m-1}{1+(m-1)a}, \tag{5.3.20}$$

for some $n = m^a$ and aim to show that

$$d_{m,k} = \frac{m-1}{1+(m-1)(a+1)} \tag{5.3.21}$$

for $k = m^{a+1}$. The main idea is to consider an optimal catalyst pair $(\omega,\omega') \in \mathscr{S}_{m,k}$ and from it construct a catalyst pair $(\sigma,\sigma') \in \mathscr{S}_{m,n}$ in dimension $n = m^a$. Since our construction will allow to relate $d(\sigma,\sigma') \geq d_{m,n}$ to $d(\omega,\omega') = d_{m,k}$, we then obtain a lower bound on $d_{m,k}$ in terms of $d_{m,n}$ as in Eq. (5.3.20).

Let us start by using the state pair that satisfies Eq. (5.3.17) and achieves $d_{m,k}$, and from it derive some useful properties. Firstly, pick $(\omega,\omega') \in \mathscr{S}_{m,k}$ so that $d(\omega,\omega') = d_{m,k}$. As before, without loss of generality, we assume that $\omega = \mathrm{diag}(\omega_1,\ldots,\omega_k)$ and $\omega' = \mathrm{diag}(\omega'_1,\ldots,\omega'_k)$ where $\omega_1 \geq \ldots \geq \omega_k$ and $\omega'_1 \geq \ldots \geq \omega'_k$. The majorization condition

$$\omega \otimes \frac{1}{m}\mathbb{I}_m \succ \omega' \otimes |0\rangle\langle 0| \;\Leftrightarrow\; \left(\frac{\omega_1}{m},\ldots,\frac{\omega_1}{m},\ldots,\frac{\omega_k}{m},\ldots,\frac{\omega_k}{m}\right) \succ (\omega'_1,\ldots,\omega'_k,0,\ldots,0) \tag{5.3.22}$$

again implies that $\omega_1 > \omega_1'$ and $\omega_i = 0$ for $i > k/m = m^a$. To further simplify matters, we can also assume that $\omega_i \leq \omega_i'$ for all $i \geq 2$. This is because we can always replace ω with $\tilde{\omega} = \mathrm{diag}(\tilde{\omega}_1, \ldots, \tilde{\omega}_k)$, where

$$\tilde{\omega}_i = \begin{cases} \omega_i' & \text{if } \omega_i > \omega_i', \\ \omega_i & \text{otherwise,} \end{cases} \tag{5.3.23}$$

for $i \geq 2$ and $\tilde{\omega}_1$ is chosen so that $\sum_i \tilde{\omega}_i = 1$. In essence, all the majorization advantage of ω against ω' can be piled upon the first, largest eigenvalue of ω. The reader is referred to Fig.5.1 for a visual comparison. This replacement is valid since $(\tilde{\omega}, \omega')$ still satisfies the majorization condition. Furthermore,

$$d(\omega, \omega') = \sum_{i:\omega_i > \omega_i'} \omega_i - \omega_i' = d(\tilde{\omega}, \omega') \tag{5.3.24}$$

implies that the distance is unchanged.

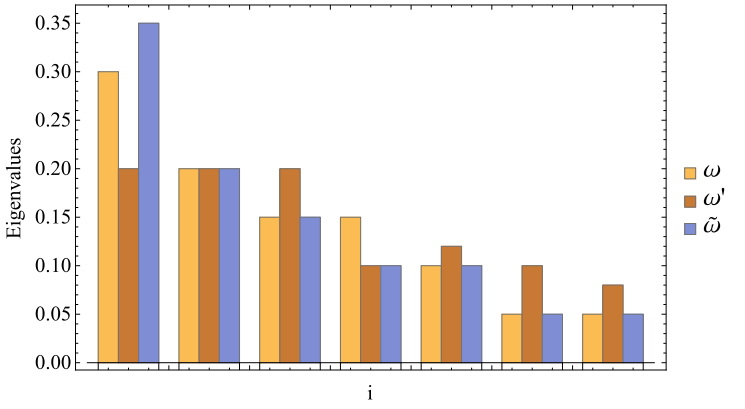

Figure 5.1: A visual comparison between an example of states ω, ω' and $\tilde{\omega}$, as defined in the proof of Theorem 5.3. We see that whenever $\omega \geq \omega'$ (yellow bar larger than brown), we can define $\tilde{\omega}$ (blue) such that $\tilde{\omega} = \omega$, and renormalize $\tilde{\omega}$ by increasing $\tilde{\omega}_1$. Also form this visualization one can observe that the trace distance as described in Eq. (5.3.24) does not change.

Subsequently, we proceed to bound $d_{m,n}$. To do this, we start from the optimal catalyst pair $(\omega, \omega') \in \mathscr{S}_{m,k}$, and construct a smaller catalyst pair $(\sigma, \sigma') \in \mathscr{S}_{m,n}$ in dimension $n = m^a = k/m$. Essentially, this is done by directly applying a cut to the dimension of the final catalyst state ω', reducing it to having dimension $k/m = n$. Similarly, the same amount of probability is cut from the initial state, and both states are renormalized.

Let us decribe this in more detail: denote $\delta = \sum_{i>k/m} \omega_i'$ and pick index s and value $\hat{\omega}_s \leq \omega_s$ so that $\sum_{i<s} \omega_i + \hat{\omega}_s = 1 - \delta$. Note that $s \leq k/m^2$, since the majorization condition Eq. (5.3.22) implies that

$$\sum_{i \leq k/m^2} \sum_{j=1}^{m} \frac{\omega_i}{m} = \sum_{i \leq k/m^2} \omega_i \geq \sum_{i \leq k/m} \omega_i' = 1 - \delta. \tag{5.3.25}$$

This inequality is obtained by summing up the first k/m elements of both distributions in the L.H.S. and R.H.S. of Eq. (5.3.22). We now define

$$\sigma = \frac{1}{1-\delta}\mathrm{diag}\big(\omega_1, \cdots, \omega_{s-1}, \hat{\omega}_s, 0, \cdots\cdots, 0\big), \tag{5.3.26}$$

$$\sigma' = \frac{1}{1-\delta}\mathrm{diag}\big(\omega'_1, \cdots, \omega'_{s-1}, \omega'_s, \omega'_{s+1}, \cdots, \omega'_{k/m}\big). \tag{5.3.27}$$

Since $\sum_{i<s}\omega_i + \hat{\omega}_s = \sum_{i\leq k/m}\omega'_i = 1-\delta$ the states σ and σ' are properly normalized. To establish that $(\sigma,\sigma') \in \mathscr{S}_{m,n}$, we need to show that the majorization condition holds true. We consider two separate cases: when $\hat{\omega}_s = \omega_s$, and when $\hat{\omega}_s \neq \omega_s$.

If $\hat{\omega}_s = \omega_s$, then the inequalities in the majorization condition for (σ,σ') have already been enforced by the majorization condition of (ω,ω'). Hence, (σ,σ') is a valid catalyst pair in dimension $n = k/m$, *i.e.*, $(\sigma,\sigma') \in \mathscr{S}_{m,k}$. Let us now make the following two observations.

1. $\boldsymbol{d(\omega,\omega') \geq \delta}$. To see this, recall that $\omega_i = 0$ for $i > k/m = n$, and thus

$$d(\omega,\omega') = \sum_{i:\omega'_i>\omega_i} \omega'_i - \omega_i \geq \sum_{i>k/m} \omega_i = \delta. \tag{5.3.28}$$

2. $\boldsymbol{d(\omega,\omega') = (1-\delta)d(\sigma,\sigma')}$. To see this, note that

$$\frac{d(\omega,\omega')}{1-\delta} = \frac{1}{1-\delta}\sum_{i:\omega_i>\omega'_i} \omega_i - \omega'_i = \frac{\omega_1-\omega'_1}{1-\delta} = d(\sigma,\sigma') \tag{5.3.29}$$

since only the first diagonal element of σ is strictly larger than the corresponding diagonal element of σ'.

Combining observations (1) and (2) gives

$$d_{m,k} = d(\omega,\omega') = (1-\delta)\cdot d(\sigma,\sigma') \geq \Big[1 - d(\omega,\omega')\Big]\cdot d(\sigma,\sigma') \geq (1-d_{m,k})\cdot d_{m,n}, \tag{5.3.30}$$

since

$$d(\sigma,\sigma') \geq d_{m,n} = \frac{m-1}{1+(m-1)a}. \tag{5.3.31}$$

Rearranging gives us

$$d_{m,k} \geq \frac{d_{m,n}}{1+d_{m,n}} = \frac{m-1}{1+(m-1)(a+1)} \tag{5.3.32}$$

and we have completed the inductive step.

If $\hat{\omega}_s \neq \omega_s$, then the majorization inequalities involving $\hat{\omega}_s$ might fail to hold. Therefore, instead of (σ,σ') we consider the following, slightly different, pair of states

$$\zeta = \sigma = \frac{1}{1-\delta}\mathrm{diag}\big(\omega_1, \cdots, \omega_{s-1}, \hat{\omega}_s, 0, \cdots, 0\big), \tag{5.3.33}$$

$$\zeta' = \frac{1}{1-\delta}\mathrm{diag}\big(\omega'_1, \cdots, \omega'_{(s-1)m}, l, \cdots, \bar{\omega}, \omega'_{sm+1}, \cdots, \omega'_{k/m}\big), \tag{5.3.34}$$

where

$$l = \frac{1}{m}\left(\omega'_{(s-1)m+1} + \ldots + \omega'_{sm}\right). \tag{5.3.35}$$

The diagonal elements of ζ' are still in descending order, and the state is properly normalized. To argue that (ζ, ζ') is a valid pair of catalyst states, we need to verify the majorization inequalities that are not directly implied by the majorization condition for (ω, ω'). That is, we need to verify that for all $1 \leq j \leq m$,

$$C + \frac{j}{m}\hat{\omega}_s \geq C' + jl, \tag{5.3.36}$$

where $C = \sum_{i=1}^{s-1} \omega_i$ and $C' = \sum_{i=1}^{(s-1)m} \omega'_i$.

We can see that this is true for (ζ, ζ') because in this regime of Eq. (5.3.36), both sides increase linearly with the indices j, and for the endpoints $j = 0$ and $j = m$, the L.H.S. is higher than the R.H.S., which is guaranteed by the majorization condition for (ω, ω'),

$$C \geq C' \quad \text{and} \quad C + \hat{\omega}_s \geq C' + ml. \tag{5.3.37}$$

Therefore, for any $0 \leq p \leq 1$, we have that

$$(1-p)C + p(C + \hat{\omega}_s) \geq (1-p)C' + p(C' + ml). \tag{5.3.38}$$

Taking $p = j/m$ yields the desired inequality (5.3.36) and hence (ζ, ζ') is a valid catalyst pair. Lastly, note that reasoning similar to the one in Eq. (5.3.29) can be used to deduce that

$$\frac{d(\omega, \omega')}{1-\delta} = d(\zeta, \zeta'). \tag{5.3.39}$$

Therefore, $d(\zeta, \zeta') = d(\sigma, \sigma')$ and we can use the argument from the previous case to complete the inductive step.

By this proof of induction we have shown that $d_{m,n} \geq m - 1/(1 + (m-1)a)$ for all $m, n = m^a$ and $a \geq 1$. This together with the conclusion in Lemma 5.2 that the quantity $d_{m,n} \leq m - 1/(1 + (m-1)a)$ proves that

$$d_{m,n} = \frac{m-1}{1 + (m-1)a}, \tag{5.3.40}$$

and the state pair described in Eq. (5.3.6) and (5.3.7) is optimal. □

Fig. 5.2 compares our final catalyst state with the state $\tilde{\omega}_C = \frac{1}{Z(n)} \sum_{j=1}^{n} \frac{1}{j} |j\rangle\langle j|$, with $Z(n) = \sum_{j=1}^{n} 1/j$ being the normalization constant, as we've seen previously in Section 5.2.1. The family $\tilde{\omega}_C$ was proposed in Ref. [144] for embezzling in the LOCC setting. In Fig. 5.3, we compare the trace distance error achieved by catalyst $\tilde{\omega}_C$ from Ref. [144] with the error achieved by our catalyst ω_C. We see that for small dimensions, our catalyst outperforms $\tilde{\omega}_C$, however asymptotically the error scales with $\log n$ for both catalysts.

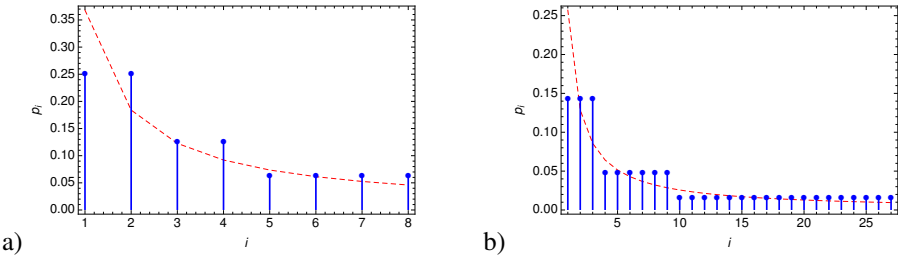

Figure 5.2: The eigenvalues of our final catalyst state ω'_C (blue) versus those of $\tilde{\omega}_C$ proposed in Ref. [144] (red, dashed), for a) $m = 2, n = 8$ and b) $m = 3, n = 27$. Similarities can be observed in the structure of both constructions.

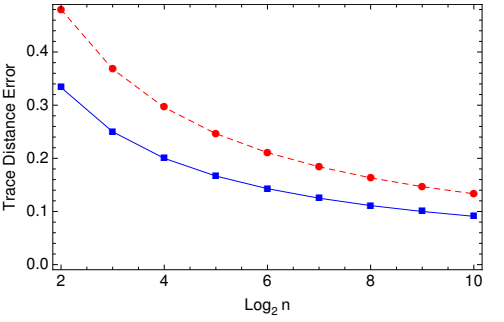

Figure 5.3: The comparison of trace distance error for our state (blue, solid) and the catalyst state in Fig. 5.2 (red, dashed), for the case where $m = 2$.

5.4. THE LIMITATIONS OF THERMAL EMBEZZLING

In this section, we investigate constraints on the catalyst that would prevent thermal embezzling with arbitrarily small error. The investigations were done for general Hamiltonians. In Section 5.4.1 we consider a dimension constraint on the catalyst, while in Section 5.4.2 we allow infinite-dimensional catalysts, but with an upper bound on the average energy.

5.4.1. DIMENSION CONSTRAINTS

BLOCK-DIAGONAL STATES

As mentioned in Lemma 5.1, given Hamiltonians $\hat{H}_S$ and $\hat{H}_C$, it suffices to consider

$$\omega_C \otimes \tau_S^\beta \xrightarrow[TO]{} \omega'_C \otimes \Pi^S_{\max}, \tag{5.4.1}$$

where the possibility of transition is governed by thermo-majorization. We prove whenever the dimension of the catalyst (and system) are finite, there exists a lower bound on the accuracy of thermal embezzling. Such a bound is dependent on $\hat{H}_S$ and $\hat{H}_C$. To do so, consider the problem

$$\begin{aligned} \varepsilon = \quad & \min \quad d(\omega_C, \omega'_C) \\ & \text{s.t.} \quad \omega_C \otimes \tau_S^\beta \to \omega'_C \otimes \Pi^S_{\max},\ 0 \le \omega, \omega' \le \mathbb{1}. \end{aligned} \tag{5.4.2}$$

In Chapter 4, we showed that for block-diagonal initial and final states ρ_S, ρ'_S, it is sufficient to consider block-diagonal catalysts. Therefore, since τ_S^β and $\Pi_{\max}^S$ are block-diagonal, it is sufficient to consider ω_C, ω'_C which are block-diagonal with respect to $\hat{H}_C$. Since all α-Rényi divergences are monotonically decreasing with thermal operations, satisfying the thermo-majorization conditions in Eq. (5.4.2) also implies that

$$D_\infty(\omega_C \otimes \tau_S^\beta \| \tau_{CS}^\beta) \geq D_\infty(\omega'_C \otimes \Pi_{\max}^S \| \tau_{CS}^\beta).$$

To simplify this expression, note that $\tau_{CS}^\beta = \tau_C^\beta \otimes \tau_S^\beta$ and that Rényi divergences are additive under tensor product. Furthermore, $D_\alpha(\rho\|\rho) = 0$ for any ρ. Therefore,

$$D_\infty(\omega_C \| \tau_C^\beta) + 0 \geq D_\infty(\omega'_C \| \tau_C^\beta) + \log \frac{Z_S}{e^{-\beta E_{\max}^S}}, \tag{5.4.3}$$

where Z_S is the partition function of the system. The eigenvalues of ω_C and ω'_C are denoted as $\{\omega_j\}$ and $\{\omega'_j\}$, respectively. Evaluting D_∞ by using the definition in Eq. 2.3.6, we obtain

$$\max_i \frac{\omega_i}{\tau_i} \geq \frac{Z_S}{e^{-\beta E_{\max}^S}} \max_j \frac{\omega'_j}{\tau_j}, \qquad \text{where } \tau_j = \frac{e^{-\beta E_j^C}}{Z_C},$$

τ_j being the eigenvalues of the thermal state for the catalyst, for the energy eigenstate with energy eigenvalue E_i^C, with normalization Z_C, the partition function of the catalyst. Therefore, we can consider a relaxation of Eq. (5.4.2),

$$\begin{aligned} \hat{\varepsilon} = \quad & \min \quad d(\omega_C, \omega'_C) \\ & \text{s.t.} \quad \max_i \frac{\omega'_i + \hat{\varepsilon}}{\tau_i} \geq \frac{Z_S}{e^{-\beta E_{\max}^S}} \max_j \frac{\omega'_j}{\tau_j}, \\ & \qquad \forall\, j,\ 0 < \omega'_j \leq 1, \end{aligned} \tag{5.4.4}$$

where $\varepsilon \geq \hat{\varepsilon}$. Since D_∞ depends only on the maximum of ω'_i/τ_i, the optimal strategy to increase D_∞ while going from ω'_C to ω_C is to increase a specific eigenvalue ω'_i by an amount $\hat{\varepsilon}$.

In the next Lemma 5.4, we show that $\varepsilon \geq \hat{\varepsilon} \geq \delta > 0$ whenever $E_{\max}^C, E_{\max}^S < \infty$.

Lemma 5.4 (Lower bound to error in catalysis)**.** *Consider $\hat{H}_S, \hat{H}_C$ finite-dimensional, and denote $\{E_i^S\}_{i=1}^m$, $\{E_i^C\}_{i=1}^n$ to be the set of energy eigenvalues respectively. Then for some fixed $E_{\max}^C, E_{\max}^S$, consider any probability distribution r (which corresponds to eigenvalues of a catalyst ω), and $\hat{\varepsilon}$ such that*

$$\max_i \frac{r_i + \hat{\varepsilon}}{\tau_i} \geq \frac{Z_S}{e^{-\beta E_{\max}^S}} \max_j \frac{r_j}{\tau_j}, \tag{5.4.5}$$

where $\tau_i = e^{-\beta E_i^C}/Z_C$. Note that index i runs over all energy levels E_i^C. Then

$$\hat{\varepsilon} \geq \left(\frac{Z_S}{e^{-\beta E_{\max}^S}} - 1 \right) \frac{e^{-\beta E_{\max}^C}}{Z_C} \neq 0. \tag{5.4.6}$$

In other words, thermal embezzling of block-diagonal states with arbitrary accuracy is not possible.

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Proof. Firstly, let r^*, τ^* indicate the eigenvalues such that $r^*/\tau^* = \max_j r_j/\tau_j$. Then

$$\max_i \frac{r_i}{\tau_i} + \max_i \frac{\hat{\varepsilon}}{\tau_i} \geq \max_i \frac{r_i + \hat{\varepsilon}}{\tau_i} \geq \frac{r^*}{\tau^*} \frac{Z_S}{e^{-\beta E^S_{\max}}}.$$

The first term of L.H.S. is equal to r^*/τ^*, and therefore can be grouped with R.H.S. to form

$$\max_i \frac{\hat{\varepsilon}}{\tau_i} \geq \frac{r^*}{\tau^*} \left(\frac{Z_S}{e^{-\beta E^S_{\max}}} - 1 \right) \geq \frac{Z_S}{e^{-\beta E^S_{\max}}} - 1,$$

where the second inequality holds since we know that $D_\infty(r\|q) = \log \max_i r_i/\tau_i = \log r^*/\tau^* \geq 0$, therefore $r^*/\tau^* \geq 1$. Finally, taking the maximization of $1/\tau_i$ over i gives $1/\tau_{\min}$, recall that τ_i corresponds to probabilities of the thermal state being in the eigenstate with energy E_i. Therefore, $\tau_{\min} = e^{-\beta E^C_{\max}}/Z_C$, and we get

$$\hat{\varepsilon} \geq \left(\frac{Z_S}{e^{-\beta E^S_{\max}}} - 1 \right) \frac{e^{-\beta E^C_{\max}}}{Z_C}. \tag{5.4.7}$$

□

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ARBITRARY STATES

The case of arbitrary states are treated separately, since our Lemma 5.1 on universal embezzlers hold only for diagonal states, where necessary and sufficient conditions are known for state transformations. Nevertheless, since the monotonicity of quantum Rényi divergences $\hat{D}_\alpha$ is still a necessary condition for arbitrary state transformations $\rho_S \xrightarrow[\text{TO}]{} \rho'_S$, one can use techniques very similar to those in Section 5.4.1 to lower bound the embezzling error.

More precisely, denote $\varepsilon(\rho_S, \rho'_S)$ to be the solution of

$$\begin{aligned} \varepsilon(\rho_S, \rho'_S) := \min \quad & d(\omega_C, \omega'_C) \\ \text{s.t.} \quad & \hat{D}_\infty(\omega_C \otimes \rho_S \| \tau^\beta_{CS}) \geq \hat{D}_\infty(\omega'_C \otimes \rho'_S \| \tau^\beta_{CS}),\ 0 \leq \omega, \omega' \leq \mathbb{1}. \end{aligned} \tag{5.4.8}$$

Recall that $\tau^\beta_{CS} = \tau^\beta_C \otimes \tau^\beta_S$, and $\hat{D}_\alpha$ is additive under tensor product. Therefore, by defining $\kappa_1(\rho_S, \rho'_S) := \hat{D}_\infty(\rho'_S \| \tau^\beta_S) - \hat{D}_\infty(\rho_S \| \tau^\beta_S)$, we can rewrite the constraint in Eq. (5.4.8)

$$\hat{D}_\infty(\omega_C \| \tau^\beta_C) \geq \hat{D}_\infty(\omega'_C | \tau^\beta_C) + \kappa_1(\rho_S, \rho'_S). \tag{5.4.9}$$

Note that this is almost equivalent to Eq. (5.4.3), except the constant $\log Z_S/e^{-\beta E^S_{\max}}$ previously is now replaced with $\kappa_1(\rho_S, \rho'_S)$. By following the same steps used to prove Lemma 5.4, we obtain a lower bound depending on ρ_S, ρ'_S.

Lemma 5.5. *Consider system and catalyst Hamiltonians which are finite-dimensional, and denote $\{E^S_i\}_{i=1}^m$ and $\{E^C_i\}_{i=1}^n$ to be the set of energy eigenvalues respectively. Then for some fixed $0 \leq E^C_{\max}, E^S_{\max} < \infty$, consider any probability distribution r (which corresponds to eigenvalues of a catalyst ω), and $\hat{\varepsilon}$ such that*

$$\max_i \frac{r_i + \hat{\varepsilon}}{\tau_i} \geq 2^{\kappa_1(\rho_S, \rho'_S)} \cdot \max_j \frac{r_j}{\tau_j},\ \forall j, 0 < r_j \leq 1, \tag{5.4.10}$$

where $\tau_i = e^{-\beta E_i^C}/Z_C$ *and* $\kappa_1(\rho_S, \rho_S') = D_\infty(\rho_S' \| \tau_S^\beta) - D_\infty(\rho_S \| \tau_S^\beta)$. *Note that index i runs over all energy levels* E_i^C. *Then*

$$\varepsilon(\rho_S, \rho_S') \geq \left[2^{\kappa_1(\rho_S, \rho_S')} - 1\right] \frac{e^{-\beta E_{\max}^C}}{Z_C} \neq 0. \tag{5.4.11}$$

This implies thermal embezzling with arbitrary accuracy, using a diagonal catalyst is not possible for any $\kappa_1(\rho_S, \rho_S') > 0$.

Comparing Lemma 5.4 and Lemma 5.5 which are very similar, one sees that for non-diagonal states Lemma 5.5 gives a state-dependent lower bound on the embezzling error. However for diagonal states, the bound in Lemma 5.4 can be made state-independent because of the existence of universal embezzlers.

5.4.2. ENERGY CONSTRAINTS

In this section, we provide lower bounds for the error in catalysis, given constraints only on the average energy of the catalyst state. We do so by fixing an upper bound on the average energy of the catalyst to the problem stated in Eq. (5.4.2). Note that this means that only infinite-dimensional catalysts are of interest, since any finite-dimensional catalyst automatically has an upper bound on its average energy.

By looking at the Rényi divergence for $\alpha = 1/2$, we can show a non-zero lower bound on the catalytic error, for cases where the partition function of the catalyst Hamiltonian Z_C is finite. This minimal assumption covers most physical scenarios, especially if we want the thermal state to be well defined. Again we start with block-diagonal states, then later generalize to arbitrary states.

BLOCK-DIAGONAL STATES

Firstly, let us recall the problem stated in Eq. (5.4.2). We aim at minimizing the trace distance between all initial and final catalyst states, such that the most significant thermal embezzlement of a smaller system S can be achieved. We denote again the block-diagonal initial and final catalysts by ω_C and ω_C' with energy eigenvalues $\{\omega_j\}$ and $\{\omega_j'\}$, so that

$$d(\omega_C, \omega_C') = \frac{1}{2} \sum_{j=1}^{\infty} |\omega_j - \omega_j'|. \tag{5.4.12}$$

By invoking only the monotonicity of $D_{1/2}$, we analyze the alternative relaxed problem

$$\begin{aligned} \min \quad & \frac{1}{2} \sum_{j=1}^{\infty} |\omega_j - \omega_j'|, \\ \text{s.t.} \quad & \sum_{j=1}^{\infty} ({\omega_j'}^{1/2} - A^{1/2} \omega_j^{1/2}) \gamma^{E_j^C} \geq 0, \ \sum_{j=1}^{\infty} \omega_j' = 1, \ \sum_{j=1}^{\infty} \omega_j = 1, \\ & \forall j, \ \omega_j', \omega_j \geq 0, \ \text{and} \ \sum_{j=1}^{\infty} E_j^C \omega_j \leq E, \end{aligned} \tag{5.4.13}$$

where

$$A = \frac{Z_S}{e^{-\beta E_{\max}^S}}, \tag{5.4.14}$$

and $\gamma = e^{-\beta/2} < 1$. Furthermore, since $A = (\min_i \tau_i)^{-1}$ with τ_i forming a probability distribution (that of a thermal state), one can deduce that whenever the dimension of system S is $m \geq 2$, $A \geq m \geq 2$ holds as well.

The solution of this minimization problem serves as a lower bound to the optimal trace distance error. This problem can be relaxed to a convex optimisation problem. We can arrive at a simple bound, however, with rather non-technical means. In essence, we introduce split bounds, so that the optimization can be written as two independent, individually significantly simpler optimization problems. We make use of the inequality

$$x^{1/2} - a^{1/2} y^{1/2} \leq |x-y|^{1/2} - f(a)y, \tag{5.4.15}$$

which holds true for $x, y \in [0,1], a \geq 2$ and with $f : \mathbb{R}^+ \to \mathbb{R}^+$ defined as

$$f(a) = \frac{1}{2}\frac{a^2}{a^2+1}. \tag{5.4.16}$$

We can then relax the problem by replacing the first constraint in Eq. (5.4.13), with x_j taking the role of $|\omega_j - \omega'_j|$, and y_j taking the role of ω_j, to arrive at

$$\begin{aligned} \min \quad & \frac{1}{2}\sum_{j=1}^{\infty} x_j, \\ \text{s.t.} \quad & \sum_{j=1}^{\infty} \left[x_j^{1/2} - f(A)\omega_j\right] e^{-\beta E_j^C/2} \geq 0, \;\; \sum_{j=1}^{\infty} \omega_j = 1, \\ & \forall j, \;\; x_j, \omega_j \geq 0 \;\text{ and }\; \sum_{j=1}^{\infty} E_j^C \omega_j \leq E. \end{aligned} \tag{5.4.17}$$

Let us first concern ourselves with the upper bound on average energy, $\sum_{j=1}^{\infty} E_j^C \omega_j \leq E$. In the next Lemma 5.6, we show that such a constraint implies that the total probability of having relatively low energy eigenvalues cannot be vanishingly small.

Lemma 5.6 (Lower bound to sums of eigenvalues)**.** *Consider any probability distribution $\{\omega_i\}$ over ascendingly ordered energy eigenvalues $\{E_i^C\}$, with the property that the energy eigenvalues are unbounded, i.e. $\lim_{n\to\infty} E_n^C = \infty$. If the expectation value of energy $\sum_{i=1}^{\infty} \omega_i E_i^C \leq E$ for some finite constant E, define for any $0 < W < 1$*

$$j(W) = \min\left\{ j : E_{j+1}^C > \frac{E}{1-W} \right\}. \tag{5.4.18}$$

Then $\sum_{i=1}^{j(W)} \omega_i \geq W$.

Proof. One can easily prove this by contradiction. Assume that $\sum_{i=1}^{j(W)} \omega_i < W$ instead, and therefore $\sum_{i=j(W)+1}^{\infty} \omega_i > 1 - W$. This violates the energy constraint, since

$$\sum_{i=j(W)+1}^{\infty} \omega_i E_i^C > (1-W)\frac{E}{1-W} = E. \tag{5.4.19}$$

□

Having established Lemma 5.6, let us return to Eq. (5.4.17). Note that this minimization can be split into two independent parts: we may first consider the subproblem of minimizing $\sum_{j=1}^{\infty} \omega_j e^{-\beta E_j^C/2}$, with respect to the constraints $\forall j, \omega_j \geq 0$ and $\sum_{j=1}^{\infty} E_j^C \omega_j \leq E$. Define ε_C to be the solution of the simple linear problem involving only variables $\{\omega_j\}$, which we explicitly write out in Corollary 5.2. One can then use Lemma 5.6 to place a lower bound on the quantity ε_C, which we detail in Corollary 5.2.

Corollary 5.2 (Lower bound to ε_C)**.** *For a set of unbounded energy eigenvalues $\{E_i^C\}$, consider the minimization problem*

$$\begin{aligned} \varepsilon_C = \min \quad & \sum_{j=1}^{\infty} \omega_j e^{-\beta E_j^C}, \\ \text{s.t.} \quad & \sum_{j=1}^{\infty} \omega_j = 1, \ \omega_j \geq 0 \ \forall j, \text{ and } \sum_{j=1}^{\infty} E_j^C \omega_j \leq E. \end{aligned}$$

Denote $\gamma = e^{-\beta} \in (0,1)$. Then for $j(W) = \min\{j : E_{j+1}^C > E/1-W\}$,

$$\varepsilon_C \geq \max_{W \in (0,1)} W \gamma^{E_{j(W)}}. \tag{5.4.20}$$

Proof. This is a direct application of Lemma 5.6, since the first and second constraints are satisfied automatically by any probability distribution. Given some $W \in (0,1)$, by Lemma 5.6 we know that $\sum_{i=1}^{j(W)} \omega_i \geq W$. The objective function then can be lower bounded as

$$\sum_{i=1}^{\infty} \omega_i e^{-\beta E_i} \geq \sum_{i=1}^{j(W)} \omega_i e^{-\beta E_{j(W)}^C} \geq W \gamma^{E_{j(W)}^C}, \tag{5.4.21}$$

for any such W. To obtain the best lower bound, one maximizes over all $W \in (0,1)$. □

Remark 5.1 (Temperature dependence)**.** *The bound obtained in Corollary 5.2 is dependent on β, the inverse temperature of the bath, and goes to zero in the limit $\beta \to \infty$.*

We have now solved the subproblem involving variables $\{\omega_i\}$. Inserting the solution into the former optimisation problem in Eq. (5.4.17), we arrive at following problem:

$$\min \frac{1}{2} \sum_{j=1}^{\infty} x_j \quad \text{s.t.} \sum_{j=1}^{\infty} x_j^{1/2} e^{-\beta E_j^C/2} \geq f(A)\varepsilon_C, \ \ \forall j, x_j \geq 0.$$

The optimal solution for this minimization can easily be lower bounded by considering the Lagrange dual, which is

$$\max \ -\frac{1}{4}\lambda^2 \sum_{j=1}^{\infty} e^{-\beta E_j^C} + \lambda f(A)\varepsilon_C, \quad \text{s. t.} \quad \lambda \geq 0.$$

In fact, this can be immediately solved as a quadratic problem for a single variable. Let

$$g(\lambda) = \sum_{j=1}^{\infty} e^{-\beta E_j^C} \lambda^2 + \lambda \varepsilon_C, \tag{5.4.22}$$

and consider the stationary point of the function by setting first derivative w.r.t. λ to zero,

$$-\frac{1}{2}\lambda\sum_i e^{-\beta E_i} + f(A)\varepsilon_C = 0, \tag{5.4.23}$$

where the second derivative is negative, hence this implies a maximum point. Substituting this into the objective function gives $f(A)\varepsilon_C^2/Z_C$, and hence we conclude that

$$\varepsilon \geq \frac{1}{2}\frac{f(A)^2\varepsilon_C^2}{Z_C}.$$

In this way, we arrive at the main result.

Theorem 5.4 (Energy constraint limits the accuracy of thermal catalysis)**.** *Consider the transformation $\omega_C \otimes \tau_S \xrightarrow[\text{TO}]{} \omega_C' \otimes |E^S_{\max}\rangle\langle E^S_{\max}|$, where $d_{\text{opt}} = d(\omega_C, \omega_C')$ is the error induced on the catalyst. Then for all catalyst states with finite average energy, d_{opt} is lower bounded by*

$$d_{\text{opt}} \quad \geq \quad \frac{1}{2}\frac{f(A)^2\varepsilon_C^2}{Z_C}, \tag{5.4.24}$$

where $f(x)$ is defined in Eq. (5.4.16), $A = Z_S/e^{-\beta E^S_{\max}}$, $\varepsilon_C = \max_{W\in(0,1)} W\gamma^{E^C_{j(W)}}$ and $j(W) = \min\{j : E^C_{j+1} > E/(1-W)\}$.
In other words, thermal embezzling of diagonal states with arbitrarily small accuracy in trace distance is not possible.

ARBITRARY STATES

Similar to discussions in Section 5.4.1 , when states ρ_S or ρ_S' are non-diagonal, we can still obtain a state dependent lower bound for the catalytic error. For any state ρ_S, ρ_S', let us define the quantity

$$\kappa_2(\rho_S, \rho_S') := \hat{D}_{1/2}(\rho_S'\|\tau_S) - \hat{D}_{1/2}(\rho_S\|\tau_S). \tag{5.4.25}$$

Then a lower bound can be obtained by following the steps as proved in Section 5.4.2, only now replacing the constant A defined in Eq. (5.4.14) with a state-dependent function.

Lemma 5.7. *For quantum states ρ_S and ρ_S', consider the transformation $\omega_C \otimes \rho_S \xrightarrow[\text{TO}]{} \omega_C' \otimes \rho_S'$, where $d_{\text{opt}} = d(\omega_C, \omega_C')$ is the error induced on the catalyst. Then for all block-diagonal catalyst states with finite average energy, d_{opt} is lower bounded by*

$$d_{\text{opt}} \quad \geq \quad \frac{1}{2}\frac{f(2^{\kappa_2(\rho_S,\rho_S')})^2\varepsilon_C^2}{Z_C},$$

where $f(x)$ is defined in Eq. (5.4.16), while the other quantities are given by

$$\kappa_2(\rho_S, \rho_S') = \hat{D}_{1/2}(\rho_S'\|\tau_S) - \hat{D}_{1/2}(\rho_S\|\tau_S),$$
$$\varepsilon_C = \max_{W\in(0,1)} W\gamma^{E^C_{j(W)}},$$
$$j(W) = \min\{j : E^C_{j+1} > E/1-W\}.$$

This implies that thermal embezzling with arbitrary accuracy, using a block-diagonal catalyst is not possible for any $\kappa_2(\rho_S, \rho_S') > 0$.

5.5. CONCLUSIONS AND OUTLOOK

In summary, in this chapter we considered inexact catalysis, where the catalyst is returned not exactly to its original state, but with some small error. We analyze how the generalized second laws change when different closeness measures are used to quantify catalytic error. In this process, we identify the problem of thermal embezzling. We carefully investigated the power and limitations of this phenomena under different physical scenarios. While this effect can be powerful in the case of fully degenerate Hamiltonians, under physically ubiquitously common settings, it is very limited. Based on the physical considerations that catalysts have non-trivial Hamiltonians, we resolve the puzzle of thermal embezzling, for all catalyst states which are block-diagonal. We summarize our findings in Table 5.2.

Energy levels of H_C \ Dimension of catalyst	Bounded	Unbounded
Fully degenerate	No	Yes
Bounded	No	Probably, true at least for fully degenerate Hamiltonians
Unbounded	N/A	No, if average energy and partition function is finite

Table 5.2: The occurance of thermal embezzling (inducing any arbitrary state transitions) with arbitrary precision, under different settings. For regimes labeled "No", explicit bounds on the trace distance error (in the catalyst) can be found in Eq. (5.3.16), Eq. (5.4.6) and Eq. (5.4.24), where these bounds are derived for the case where initial/final states of the system are block-diagonal.

The bounds on dimensionality are closely related to energy restrictions. While placing an upper bound on the dimension directly imply an upper bound on the average energy, the reverse statement is not generally true. However, if one restricts not only the expectation value of the energy distribution, but also restricts its variance to be finite, then this is almost equivalent to placing a dimension restriction. For example, given any non-degenerate Hamiltonian $\hat{H}_C$ with unbounded eigenvalues, consider the set of catalyst states such that the average energy and variance of a given catalyst is finite. Then by the Chebyshev inequality [69], one can understand that this is equivalent to introducing a cut-off on the maximum energy eigenvalue (and therefore on the dimension).

For infinite-dimensional Hamiltonians, we have shown that for certain classes of catalyst Hamiltonians, explicit bounds can be derived on the trace distance error of a catalyst when the average energy is finite. Our results have covered a large range of Hamiltonians which are commonly found in physical systems - including the important case of the harmonic oscillator in free systems - with the minimal assumption that partition function Z_C is

finite, which holds for all systems for which the Gibbs thermal state is well-defined. However, we know that thermal embezzling can be arbitrarily accurate as dimension grows, at least in the simplest case of the trivial Hamiltonian. This implies that there will be specific cases of infinite-dimensional Hamiltonians where simply bounds on average energy do not give explicit bounds on thermal embezzling error. We suspect that this may be true for systems with unbounded dimension, but bounded Hamiltonians. The reason is that if dimension is unbounded, then there must exist an accumulation point in the energy spectrum. The subspace of this accumulation point will be very similar to the trivial Hamiltonian.

6

HEAT ENGINES: FROM CLASSICAL TO QUANTUM

Sadi Carnot's theorem regarding the maximum efficiency of heat engines is considered to be of fundamental importance in thermodynamics. This theorem famously states that the maximum efficiency depends only on the temperature of the heat baths used by the engine - but not the specific details on how these baths are actually realized. Carnot's results can be derived as a consequence of the second law of thermodynamics. Given that the second law has to be refined in the quantum microscopic regime, how does that affect the fundamental performance of a quantum heat engine? Furthermore, a suitable way of quantifying work for microscopic quantum systems has been constantly debated in the field of quantum thermodynamics. Can we find a characterization of work that justifies the energy extracted from a quantum heat engine? To address these questions, in this chapter we build a model for a generic quantum heat engine, and propose three different characterizations of work: perfect, near perfect and imperfect work. We demonstrate that in the regime where only the macroscopic second law matters, then Carnot's result may be recovered in such a heat engine setup.

6.1. INTRODUCTION

In this chapter, we turn to look at heat engines, which are systems designed in order to convert heat or thermal energy into usable, often either chemical energy which is stored up, or directly into mechanical work. Throughout the past century, countless efforts have been poured into designing explicit (classical) heat engines that perform at a high efficiency, or high power. Although the intricacies of materials and engineering designs may affect the performance of a heat engine from a practical level, ultimately there are fundamental limitations that are universal for all heat engines possibly conceived of. In the classical realm of thermodynamics, such fundamental features have been outlined by the works of Carnot, Kelvin, Clausius, and other physicists/engineers less known for their work on thermodynamics, such as Helmholtz, Otto, etc.

6.1.1. HEAT ENGINES: A CLASSICAL BACKGROUND

Nicolas Léonard Sadi Carnot is often described as the "father of thermodynamics". In his only publication in 1824 [150], Carnot gave the first successful theory of the maximum efficiency of heat engines. It was later used by Rudolf Clausius and Lord Kelvin to formalize the second law of thermodynamics and define the concept of entropy [151, 152]. Carnot concluded that the maximum efficiency did not depend upon the exact nature of the working fluids. He stated this for emphasis as a general proposition in [150]:

> *The motive power of heat is independent of the agents employed to realize it; its quantity is fixed solely by the temperatures of the bodies between which is effected, finally, the transfer of caloric.*

For his "motive power of heat", we would today say "the efficiency of a reversible heat engine", and rather than "transfer of caloric" we would say "the reversible transfer of heat." *Working fluids* refers to the substance (normally gas or liquid) which constitutes the thermal reservoir, which are at fixed temperatures. Carnot defined a hypothetical heat engine (now known as the *Carnot engine*) which would achieve the maximum efficiency. By using reversibility arguments according to the classical second law, he showd that such a reversible engine would attain the maximum efficiency. Later, this efficiency - now known as the Carnot efficiency (CE) - was shown to be

$$\eta_C = 1 - \frac{\beta_{\text{Hot}}}{\beta_{\text{Cold}}}, \tag{6.1.1}$$

where β_{Cold}, β_{Hot} are the inverse temperatures of the cold and hot baths respectively.

As the variety of heat engines have increased by day, the variation in size has also widened. From the steam engine and heat pumps of the 19th century, we have moved on to the design of mesoscopic machines for biomedical purposes [11, 153]. Such machines include a whole variety of molecular motors functioning on the basis of Brownian theory of motion [13]. Even in this classical regime, the fundamentals of classical thermodynamics break down due to the fact that energy fluctuations become non-negligible [154]. As studies have rightly noted, the results of such fluctuations are the signature of small engines, which are absent in the macroscopic regime. This already hints at the need of a refined understanding of thermodynamics, as we attempt to adapt it to the quantum microregime.

6.1.2. QUANTUM HEAT ENGINES (QHES)

Recent advancements in the engineering and control of quantum systems, have further pushed the applicability of conventional thermodynamics to its limits. Unlike the large scale heat engines that inspired thermodynamics, we are now able to built nanoscale quantum machines consisting of a mere handful of particles, prompting many efforts to understand quantum thermodynamics [45, 91, 92, 108, 117, 123–125, 127, 155–161]. Such studies are highly motivated by the prospects of designing small, energy efficient machines applicable to state-of-the-art devices, particularly those relevant for quantum computing and information processing. Such devices are too small to admit statistical methods, and the workings of thermodynamics become more intricate in such regimes [45, 91, 108, 125, 159]. On the other hand, coherences and entanglement which are present in quantum mechanics, have no analog in the classical world.

Quantum heat engines (QHE) are therefore machines that perform the task of work extraction when the involved systems are not only extremely small in size/particle numbers, but also subjected to the laws of quantum physics. The question then arises: how efficient can these machines be?

Recently, a number of schemes for QHEs have been proposed and analyzed, involving systems such as ion traps, photocells, or optomechanical systems [126, 160, 162–167]. Some of these schemes lie outside the usual definition of a heat engine (see Fig. 6.1). For example, instead of the engine using a hot and cold bath, the extended quantum heat engine (EQHE) has access to reservoirs which are not in a thermal state [20, 156, 160]. In this case, EQHE with high efficiencies (even surpassing η_C) have been proposed and demonstrated. Nevertheless, [161] has pointed out that the second law is, strictly speaking, never violated for such EQHEs because one always has to invest extra work in order to create and replenish these special non-thermal reservoir states. In contrast, in this chapter we consider the standard setting of a quantum heat engine, in which the baths are indeed thermal. We have seen in Chapter 4 that the laws of thermodynamics for small quantum systems are more restrictive due to finite-size effects. It turns out that such laws introduce additional restrictions on the performance of QHEs [168]. Furthermore, considering a probabilistic approach towards work extraction, [169] found that the achievement of Carnot efficiency is a very unlikely event, when considering energy fluctuations in the microregime.

Can we design a QHE that operates between genuinely thermal reservoirs and yet achieves a high efficiency? To answer this question, several protocols have been proposed [126, 170] and analyzed, showing that they operate at the Carnot efficiency. Crucial to these results is the definition of work, where we have discussed briefly in Chapter 3. In these approaches, the most common approach of quantifying work is to measure the average increase in energy of an ancillary system, sometimes referred to as the battery, after a certain work extraction protocol [126, 127, 171–173]. The quality of work extracted is usually argued to be good by quantifying higher moments of the energy distribution, or by restricting the amount of entropy to be low. However, while such approaches limit the amount of heat contribution to the energy extracted, they do not completely prevent it. What's more, no justification goes into using such a definition of work. A universally agreed upon definition of performing microscopic work is lacking, and it remains a constantly debated subject in the field of quantum thermodynamics [108, 122–124, 173]. This is mainly why a complete picture describing the performance limits of a QHE remains unknown.

6.1.3. RESULTS AND CONTRIBUTIONS

The goal of this chapter is to adopt the theoretical framework of catalytic thermal operations in order to describe a heat engine in full generality. We highlight the following steps achieved, which form the basis for Chapter 7.

- We start from the most basic conceptual model of a heat engine, and identify the role of each components in a resource theoretic framework.
- We discuss the quantification of extracted work, and provide a way to classify the quality of work according to the (relative) amount of entropy produced and stored in the energy output. We distinguish three types of work: perfect, near perfect and imperfect work.
- Using our setup, we derive the maximum attainable efficiency of a heat engine according to the standard second law. We arrive at Carnot's statement in full mathematical rigour, for the extraction of both perfect and near perfect work.

6.1.4. CHAPTER OUTLINE

Sections 6.2 and 6.3 lay the main framework for our analysis. The generic setup of a QHE is described with full rigour in Section 6.2, while different characterizations of work is discussed in Section 6.3. With these foundations to steer our analysis, we apply the second laws derived in Chapter 4 to find the amount of extractable work in such a QHE. Section 6.4.1 does this assuming only the macroscopic second law holds, while in Section 6.4.2 we derive the maximum extractable work according to all the generalized second laws.

In Section 6.5 we turn to the central quantity of interest, namely the efficiency of a QHE. Section 6.5.1 gives the formal definition of this quantity, while 6.5.2 shows that under certain assumptions, a simplified expression can be derived for efficiency, which depends explicitly only on the final state of the cold bath.

Before we move on to Chapter 7, in Section 6.6, we first use our setup and derive the maximum efficiency by considering only the standard second law. Here, we show that the classically known result for maximum efficiency can be derived in this model, according to the standard second law for both perfect work and near perfect work. We spell out rigorous derivations of some thermodynamic identities, which will also be useful later in Chapter 7.

6.2. A GENERIC SETUP FOR QUANTUM HEAT ENGINES

Let us first describe a generic QHE, which is in essence, a procedure for extracting work from two thermal baths at a temperature difference. The basic components of a QHE are detailed in Fig. 6.1. Such an engine comprises of four basic elements: two thermal baths at distinct temperatures, a machine, and a battery. The machine interacts with these baths in such a way that utilizes the temperature difference between the two baths to perform work extraction. The extracted work can then be transferred and stored in the battery, while the machine returns to its original state. The total Hamiltonian

$$\hat{H}_t = \hat{H}_{\text{Cold}} + \hat{H}_{\text{Hot}} + \hat{H}_{\text{M}} + \hat{H}_{\text{W}}, \tag{6.2.1}$$

is the sum of each individual Hamiltonian, where the indices Hot, Cold, M, W represent a hot thermal bath (Hot), a cold thermal bath (Cold), a machine (M), and a battery (W)

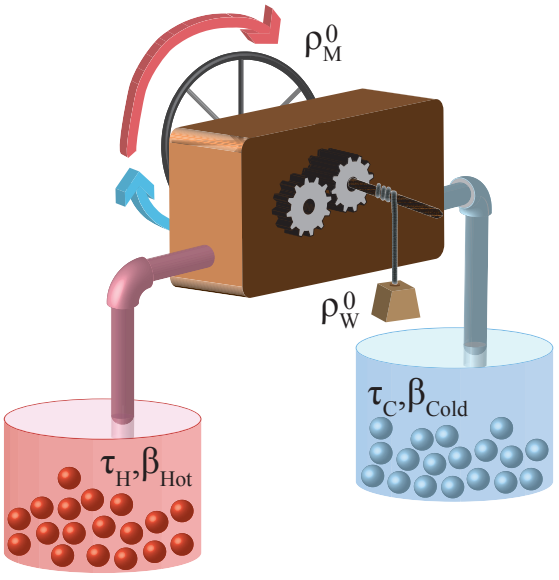

Figure 6.1: **A heat engine** extracts work from the temperature difference of a hot bath (red) at inverse temperature β_h and cold bath (blue) at inverse temperature β_c. The term bath indicates that the initial states of these systems are thermal, $\tau_{\text{Hot}}^{\beta_h} = \exp(-\beta_h \hat{H}_{\text{Hot}})/Z_{\text{Hot}}^{\beta_h}$ and $\tau_{\text{Cold}}^{\beta_c} = \exp(-\beta_c \hat{H}_{\text{Cold}})/Z_{\text{Cold}}^{\beta_c}$ with inverse temperatures β_h and β_c, and partition functions $Z_{\text{Hot}}^{\beta_h}$ and $Z_{\text{Cold}}^{\beta_c}$ respectively. The machine itself corresponds to a quantum system M with Hamiltonian $\hat{H}_{\text{M}}$, starting in an arbitrary state ρ_{M}. The battery indicates the system on which work is extracted and stored as energy. Let ρ_{W}^0 denote the initial state of the work system, and $\hat{H}_{\text{W}}$ its Hamiltonian. Operating the entire heat engine for one cycle corresponds to applying a global unitary transform U across both baths, the actual machine, and the work system. In order to account for all energy transfers we will thereby demand that $[U, \hat{H}] = 0$, where $\hat{H} = \hat{H}_{\text{M}} + \hat{H}_{\text{Cold}} + \hat{H}_{\text{Hot}} + \hat{H}_{\text{W}}$. That is, U conserves total energy.

respectively. Let us also consider an initial state

$$\rho^0_{\text{ColdHotMW}} = \tau^0_{\text{Cold}} \otimes \tau^0_{\text{Hot}} \otimes \rho^0_{\text{M}} \otimes \rho^0_{\text{W}}. \tag{6.2.2}$$

We assume the systems were initially brought together in an uncorrelated fashion, because they have not interacted with each other beforehand. The state τ^0_{Hot} (τ^0_{Cold}) is the initial thermal state at inverse temperature β_h (β_c), corresponding to the hot (cold) bath Hamiltonian $\hat{H}_{\text{Hot}}$($\hat{H}_{\text{Cold}}$), and $\beta_h < \beta_c$. The initial machine $(\rho^0_{\text{M}}, \hat{H}_{\text{M}})$ can be chosen arbitrarily, as long as its final state is preserved (and therefore the machine acts like a catalyst).

We adopt the resource theory approach by allowing all unitaries U on the global system such that $[U, \hat{H}_{\text{ColdHotMW}}] = 0$. If $(\tau^0_{\text{Hot}}, \hat{H}_{\text{Hot}})$ and $(\rho^0_{\text{M}}, \hat{H}_{\text{M}})$ can be arbitrarily chosen, then any such unitary U, $(\tau^0_{\text{Hot}}, \hat{H}_{\text{Hot}})$ and $(\rho^0_{\text{M}}, \hat{H}_{\text{M}})$ defines a *catalytic thermal operation* which one can perform on the joint state ColdW. This implies that the cold bath is used as a non-thermal resource, relative to the hot bath. By catalytic thermal operations that act on the cold bath, using the hot bath as a thermal reservoir, and the machine as a catalyst, one can extract work and store it in the battery. The aim is to achieve a final *reduced* state $\rho^1_{\text{ColdHotMW}}$, such that

$$\rho^1_{\text{ColdMW}} = \text{tr}_{\text{Hot}}(\rho^1_{\text{ColdHotMW}}) = \rho^1_{\text{ColdW}} \otimes \rho^1_{\text{M}}, \tag{6.2.3}$$

where $\rho^1_{\text{M}} = \rho^0_{\text{M}}$, and ρ^1_{Cold} is the final joint state of the cold bath and battery.

Finally, we describe the battery such that the state transition $\rho^0_{\text{ColdW}} \xrightarrow[\text{CTO}]{} \rho^1_{\text{ColdW}}$ stores work in the battery. To do so, consider the battery with Hamiltonian

$$\hat{H}_{\text{W}} := \sum_{i=1}^{n_{\text{W}}} E^{\text{W}}_i |E_i\rangle\langle E_i|_{\text{W}}. \tag{6.2.4}$$

For some parameter $\varepsilon \in [0, 1)$, we consider the initial and final states of the battery to be

$$\rho^0_{\text{W}} = |E_j\rangle\langle E_j|_{\text{W}}, \tag{6.2.5}$$

$$\rho^1_{\text{W}} = (1-\varepsilon)|E_k\rangle\langle E_k|_{\text{W}} + \varepsilon|E_j\rangle\langle E_j|_{\text{W}}, \tag{6.2.6}$$

respectively. The extracted work during a transformation W_{ext} is defined as

$$W_{\text{ext}} := E^{\text{W}}_k - E^{\text{W}}_j. \tag{6.2.7}$$

where we define $E^{\text{W}}_k > E^{\text{W}}_j$ so that $W_{\text{ext}} > 0$. The parameter ε corresponds to the failure probability of extracting work, usually chosen to be small.

To summarize, so far we have made the following minimal assumptions:

(A.1) Product state: There are no initial correlations between the cold bath, machine and battery. Initial correlations we assume do not exist, since each of the initial systems are brought independently into the process. This is an advantage of our setup, since if one assumed initial correlations, one would then have to use unknown resources to generate them in the first place.

(A.2) Perfect cyclicity: The machine undergoes a cyclic process, i.e. $\rho_{\mathrm{M}}^{0} = \rho_{\mathrm{M}}^{1}$, and is also not correlated with the rest of the cold bath and battery, as described in Eq. (6.2.3). This is to ensure that the machine does not get compromised in the process: since if ρ_{M}^{0} was initially correlated with some reference system R, then by monogamy of entanglement, correlations between ρ_{M}^{1} and $\rho_{\mathrm{ColdW}}^{1}$ would potentially destroy such correlations between the machine M with R. Later on, we consider in Chapter 7 a relaxation, where the machine is allowed to be correlated with the battery and bath as well, as long as the reduced state $\rho_{\mathrm{M}}^{1} = \rho_{\mathrm{M}}^{0}$ remains unchanged. We will see that this does not affect the results of our analysis.

(A.3) Isolated quantum system: The heat engine as a whole, is isolated from and does not interact with the world. This assumption ensures that all possible resources in a work extraction process have been accounted for.

(A.4) Finite dimension: The Hilbert space associated with $\rho_{\mathrm{ColdHotMW}}^{0}$ is finite dimensional but can be arbitrarily large. Moreover, the Hamiltonians $\hat{H}_{\mathrm{Cold}}$, $\hat{H}_{\mathrm{Hot}}$, $\hat{H}_{\mathrm{M}}$ and $\hat{H}_{\mathrm{W}}$ all have bounded pure point spectra, meaning that these Hamiltonians have eigenvalues which are bounded.

Let us also define the notion of a *quasi-static* heat engine, which will be important in our analysis.

Definition 6.1. *(Quasi-static [168]) A heat engine is* quasi-static *if the final state of the cold bath is a thermal state and its inverse temperature β_f only differs infinitesimally from the initial cold bath temperature, i.e. $\beta_f = \beta_c - g$, where $0 < g \ll 1$. We also refer to g as the quasi-static parameter.*

6.3. PERFECT, NEAR PERFECT AND IMPERFECT WORK

The definition of work when dealing with nanoscale quantum systems has seen much attention lately [45, 91, 108, 123–125]. As we have seen in Chapter 3, work is always understood as changing the energy of a system, which we call *battery*.

One aspect of extracting work W is to bring the battery's initial state ρ_{W}^{0} to some final state ρ_{W}^{1} such that $W = \mathrm{tr}(\rho_{\mathrm{W}}^{1}\hat{H}_{\mathrm{W}}) - \mathrm{tr}(\rho_{\mathrm{W}}^{0}\hat{H}_{\mathrm{W}}) > 0$. However, a change in average energy alone, does not yet correspond to performing work. It is implicit in our macroscopic understanding of work that the energy transfer takes place in an ordered form. When lifting a weight, we *know* its final position and can exploit this precise knowledge to transfer all the work onto a third system without - in principle - losing any energy in the process. In the quantum regime, such knowledge corresponds to ρ_{W}^{1} being a pure state; and when ρ_{W}^{1} is diagonal, then ρ_{W}^{1} is an energy eigenstate. We can thus understand work as an energy transfer about which we have perfect information, while heat, in contrast, is an energy transfer about which we hold essentially no information. Clearly, there is also an intermediary regime in which we transfer energy, while having some - but not perfect - information.

To illustrate this idea, consider a two-level system battery, where we extract work by transiting from an initial energy eigenstate $|E_{\mathrm{W}}^{j}\rangle\langle E_{\mathrm{W}}^{j}|$ to another energy eigenstate $|E_{\mathrm{W}}^{k}\rangle\langle E_{\mathrm{W}}^{k}|$, where $E_{\mathrm{W}}^{k} - E_{\mathrm{W}}^{j} > 0$. Changing the energy, while having some amount of information corre-

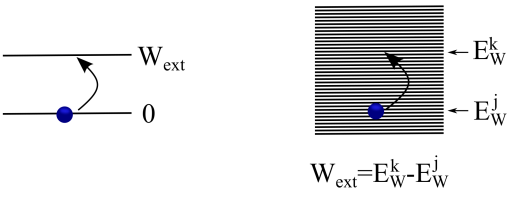

Figure 6.2: **A battery** is a work-storage component of a heat engine. In the nanoscale regime, a minimal way of modeling the battery is as a two-level system [125] . Performing work corresponds to "lifting" the state from ground state to the excited state, where the energy gap is fine-tuned to the amount of work W_{ext} to be done. While an arbitrary energy spacing is difficult to realize in a two-level system, it can be done by picking two levels with the desired spacing from a quasi-continuum battery: this battery comprises of a large but finite number of discrete levels which form a quasi-continuum. Such a battery closely resembles the classical notion of a "weight attached to a string" as considered in [126] . The battery can be charged from a particular state (e.g. the ground state) to any of the higher levels.

sponds to changing the state of the battery to a mixture $\rho_{\text{W}}^1 = (1-\varepsilon)|E_{\text{W}}^k\rangle\langle E_{\text{W}}^k| + \varepsilon|E_{\text{W}}^j\rangle\langle E_{\text{W}}^j|$ for some parameter $\varepsilon \in [0,1]$. The case of $\varepsilon = 0$ corresponds to doing *perfect work*.

The smaller ε is, the closer we are to the situation of perfect work. One can characterize this intermediary regime by the von Neumann entropy $S(\rho_{\text{W}}^1)$. For perfect work, $S(\rho_{\text{W}}^1) = 0$, while for heat transfer (thermalization), under a fixed average energy, the two-level battery becomes thermal, since the thermal state maximizes entropy for a fixed energy [23].

When $\varepsilon > 0$, what is relevant is not ε as an absolute, but relative to the energy extracted W_{ext}. We are thus interested in $\Delta S / W_{\text{ext}}$ where

$$\Delta S := S(\rho_{\text{W}}^1) - S(\rho_{\text{W}}^0) \tag{6.3.1}$$

is the change in entropy of the battery. We categorize work into the following regimes:

Definition 6.2. *(Perfect work) An amount of work extracted W_{ext} is referred to as* perfect work *when $\varepsilon = 0$.*

Definition 6.3. *(Near perfect work) An amount of work extracted W_{ext} is referred to as* near perfect work *when*

1) $0 < \varepsilon \leq l$, for some fixed $l < 1$ and

2) $0 < \dfrac{\Delta S}{W_{\text{ext}}} < p$ for any $p > 0$, i.e. $\dfrac{\Delta S}{W_{\text{ext}}}$ is arbitrarily small.

When W_{ext} is finite, items 1) and 2) are both satisfied only in the limit $\varepsilon \to 0$, iff

$$\lim_{\varepsilon \to 0^+} \frac{\Delta S}{W_{\text{ext}}} = 0. \tag{6.3.2}$$

Definition 6.4. *(Imperfect work) An amount of work extracted W_{ext} is referred to as* imperfect work *when*

1) $0 < \varepsilon \leq l$, for some fixed $l < 1$ and

2) $\frac{\Delta S}{W_{\text{ext}}} = p$ for some value $p > 0$, i.e. $\frac{\Delta S}{W_{\text{ext}}}$ is lower bounded away from zero.

The limit of $\varepsilon \to 0$ will be the focus of our analysis, for several reasons. Firstly, for any finite amount of near perfect work extraction, ε should be arbitrarily small, as we have seen in Def. 6.3. On the other hand, we show that the Carnot efficiency is achieved in the quasi-static limit, i.e. $g \to 0$. In this limit, since the cold bath does not change, the amount of work extractable W_{ext} is infinitesimal. Furthermore, recall that one is interested not in the absolute values of ΔS, but the ratio $\frac{\Delta S}{W_{\text{ext}}}$, for most cases of imperfect work (when the ratio of $\frac{\Delta S}{W_{\text{ext}}}$ is finite) we know that ΔS is vanishingly small, and therefore so is ε.

6.4. CONDITIONS FOR WORK EXTRACTION

In this section, we briefly state the laws that govern the transition $\rho^0_{\text{ColdHotMW}} \to \rho^1_{\text{ColdHotMW}}$ for one cycle of our heat engine. By applying these laws, the amount of extractable work W_{ext} can be quantified and expressed as a function of the cold bath.

6.4.1. SECOND LAW FOR MACROSCOPIC SYSTEMS

Let us first recall what conventional thermodynamics predict about how much work is extractable. The cold bath, machine and battery form a *closed* but not isolated thermodynamic system. This means only heat exchange (and not mass exchange) occurs between these systems and the hot bath. Therefore, a transition from ρ^0_{ColdMW} to ρ^1_{ColdMW} will be possible if and only if the Helmholtz free energy, F does not increase

$$F(\rho^0_{\text{ColdMW}}) \geq F(\rho^1_{\text{ColdMW}}), \tag{6.4.1}$$

where

$$F(\rho) := \langle \hat{H} \rangle_\rho - \frac{1}{\beta} S(\rho), \tag{6.4.2}$$

and $S(\rho) := -\mathrm{tr}(\rho \ln \rho)$ and $\langle \hat{H} \rangle_\rho := \mathrm{tr}(\hat{H}\rho)$ being the entropy and the mean energy of state ρ respectively. Throughout the chapter, whenever the state is a thermal state at temperature β, we use the shorthand notation $\langle \hat{H}_{\text{Cold}} \rangle_\beta$ and $S(\beta)$.

The Helmholtz free energy bears a close relation to the *relative entropy* which we have defined in Eq. (2.3.11). Whenever ρ and σ are diagonal in the same basis,

$$D(\rho \| \sigma) = \sum_i p_i \ln \frac{p_i}{q_i}, \tag{6.4.3}$$

where p_i, q_i are the eigenvalues of ρ and σ respectively. Now, for any Hamiltonian $\hat{H}$, consider $\tau^\beta = \mathrm{e}^{-\beta\hat{H}}/Z_\beta$, which is the thermal state at some inverse temperature β, with partition function $Z_\beta = \mathrm{tr}[\mathrm{e}^{-\beta\hat{H}}]$, and denote its eigenvalues as q_i. Then for any diagonal state ρ with eigenvalues p_i, and denoting $\{E_i\}_i$ as the eigenvalues of $\hat{H}$,

$$D(\rho\|\tau^\beta) = \sum_i p_i \ln\frac{p_i}{q_i} = -S(\rho) + \sum_i p_i(\beta E_i + \ln Z_\beta) = \beta F(\rho) + \ln Z_\beta. \tag{6.4.4}$$

This implies that

$$F(\rho) = \frac{1}{\beta}[D(\rho\|\tau^\beta) - \ln Z_\beta]. \tag{6.4.5}$$

6.4.2. SECOND LAWS FOR NANOSCOPIC SYSTEMS

In the microscopic quantum regime, where only a few quantum particles are involved, it has been shown in Chapter 4 that macroscopic thermodynamics is not a complete description of thermodynamical transitions. More precisely, not only the Helmholtz free energy, but a whole other family of generalized free energies have to decrease during a state transition. This places further constraints on whether a particular transition is allowed. In particular, these laws also give necessary and sufficient conditions, when a system with initial state ρ^0_{ColdW} can be transformed to final state ρ^1_{ColdW} (both block-diagonal), with the help of any catalyst/machine which is returned to its initial state after the process.

We can apply these second laws to our scenario by associating the catalyst with ρ^0_{M}, and considering the state transition $\rho^0_{\mathrm{W}} \otimes \tau^0_{\mathrm{Cold}} \xrightarrow[\mathrm{CTO}]{} \rho^1_{\mathrm{W}} \otimes \rho^1_{\mathrm{Cold}}$ as described in Section 6.2. Note that the initial state $\rho^0_{\mathrm{W}} \otimes \tau^0_{\mathrm{Cold}}$ is block-diagonal in the energy eigenbasis (for the battery by our choice, and for the cold bath because it is a thermal state). By catalytic thermal operations, the final state is also block-diagonal in the energy eigenbasis. Furthermore, according to Theorem 4.5 in Chapter 4, the transition from $\rho^0_{\mathrm{W}} \otimes \tau^0_{\mathrm{Cold}} \xrightarrow[\mathrm{CTO}]{} \rho^1_{\mathrm{W}} \otimes \rho^1_{\mathrm{Cold}}$ is then possible iff

$$F_\alpha(\tau^0_{\mathrm{Cold}} \otimes \rho^0_{\mathrm{W}}, \tau^h_{\mathrm{ColdW}}) \geq F_\alpha(\rho^1_{\mathrm{Cold}} \otimes \rho^1_{\mathrm{W}}, \tau^h_{\mathrm{ColdW}}) \quad \forall \alpha \geq 0, \tag{6.4.6}$$

where τ^h_{ColdW} is the thermal state of the system at inverse temperature β_h of the surrounding bath. On occasion, we will refer to a particular transition as being possible/impossible according to the F_α free energy constraint. By this, we mean that for that particular value of α and transition, Eq. (6.4.6) is satisfied/not satisfied.

The reader should note that for both Section 6.4.1 and 6.4.2, the conditions for state transformation place upper bounds on the quantity W_{ext}. In particular, this allows us to express the maximum values W_{ext} can take (such that the joint state transformation of cold bath and battery is possible) in terms of quantities related to the cold bath, and the error probability ε. It is also worth comparing the conditions for state transformation in Section 6.4.1 and 6.4.2, which are stated in Eqs. (6.4.1) and (6.4.6). In particular, Eq. (6.4.1) is but a particular instance of Eq. (6.4.6), and therefore the nanoscopic second laws always place a stronger upper bound on W_{ext} compared to the macroscopic second law.

6.5. EFFICIENCY OF HEAT ENGINES

6.5.1. DEFINITIONS

Given the initial and final states $\rho^0_{\text{ColdHotMW}}, \rho^1_{\text{ColdHotMW}}$ that define a particular heat engine, the efficiency is defined as

$$\eta := \frac{W_{\text{ext}}}{\Delta H}, \tag{6.5.1}$$

where W_{ext} is the amount of work extracted which is defined in Eq. (6.2.7), and ΔH is the amount of mean energy drawn from the hot bath, namely $\Delta H := \text{tr}(\hat{H}_{\text{Hot}}\rho^0_{\text{Hot}}) - \text{tr}(\hat{H}_{\text{Hot}}\rho^1_{\text{Hot}})$, where ρ^1_{Hot} is the reduced state of the hot bath.

Now, consider the set of conditions on state transformations given by Eq. (6.4.6) for nanoscale systems. These conditions place a restriction on the range of values W_{ext} can take. Therefore, for any fixed ρ^1_{Cold}, we define $\eta^{\text{nano}}(\rho^1_{\text{Cold}})$ as the maximum achievable efficiency as a function of the final state of the cold bath. More precisely,

$$\begin{aligned} &\eta^{\text{nano}}(\rho^1_{\text{Cold}}) \\ &= \sup_{W_{\text{ext}}} \eta(\rho^1_{\text{Cold}}) \quad \text{s.t.} \quad F_\alpha(\rho^0_{\text{W}} \otimes \tau^0_{\text{Cold}}, \tau^h_{\text{ColdW}}) \geq F_\alpha(\rho^1_{\text{W}} \otimes \rho^1_{\text{Cold}}, \tau^h_{\text{ColdW}}) \quad \forall \alpha \geq 0. \end{aligned} \tag{6.5.2}$$

In Eq. (6.5.2), each quantity expect for $\rho^1_{\text{Cold}}$is fixed (recall that the states $\rho^0_{\text{W}}, \rho^1_{\text{W}}$ are fixed according to Eq. (6.2.5) and (6.2.6)), therefore we have written the quantity in Eq. (6.5.1) as $\eta = \eta(\rho^1_{\text{Cold}})$ to remind ourselves of this explicit dependency. Therefore, the maximum efficiency will correspond to maximizing over the final state of the cold bath:

$$\eta^{\text{nano}}_{\text{max}} = \sup_{\rho^1_{\text{Cold}} \in S(\mathscr{H}_{\text{Cold}})} \eta^{\text{nano}}(\rho^1_{\text{Cold}}), \tag{6.5.3}$$

where $S(\mathscr{H}_{\text{Cold}})$ is the space of all quantum states in $\mathscr{H}_{\text{Cold}}$.

In the macroregime, we have to satisfy a less stringent requirement, namely the macroscopic second law of thermodynamics. And hence we have that for fixed ρ^1_{Cold}, $\eta^{\text{mac}}(\rho^1_{\text{Cold}})$ is the maximum efficiency as a function of ρ^1_{Cold}

$$\eta^{\text{mac}}(\rho^1_{\text{Cold}}) = \sup_{W_{\text{ext}}} \eta(\rho^1_{\text{Cold}}) \quad \text{s.t.} \quad F(\rho^0_{\text{ColdMW}}) \geq F(\rho^1_{\text{ColdMW}}) \tag{6.5.4}$$

$$\text{and} \quad \text{tr}(\hat{H}_t \rho^0_{\text{ColdHotMW}}) = \text{tr}(\hat{H}_t \rho^1_{\text{ColdHotMW}}), \tag{6.5.5}$$

where $\hat{H}_{\text{ColdHotMW}}$ is defined in Eq. (6.2.1). Similarly to the nanoscale setting, the maximum efficiency is

$$\eta^{\text{mac}}_{\text{max}} = \sup_{\rho^1_{\text{Cold}} \in S(\mathscr{H}_{\text{Cold}})} \eta^{\text{mac}}(\rho^1_{\text{Cold}}). \tag{6.5.6}$$

We can also define the maximum quasi-static efficiencies for the macro and nano scale. The maximum efficiency of a quasi-static heat engine (see Def. 6.1), is

$$\eta^{\text{stat,nano}}_{\text{max}} = \lim_{g \to 0^+} \eta^{\text{nano}}(\tau(g)), \tag{6.5.7}$$

$$\eta^{\text{stat,mac}}_{\text{max}} = \lim_{g \to 0^+} \eta^{\text{mac}}(\tau(g)), \tag{6.5.8}$$

for the *nanoscopic* and *macroscopic* cases respectively. The state $\tau(g) \in \mathscr{H}_{\text{Cold}}$ is the thermal state with Hamiltonian $\hat{H}_{\text{Cold}}$ at temperature $\beta_f = \beta_c - g$ and $\eta^{\text{nano}}, \eta^{\text{mac}}$ are defined in Eqs. (6.5.2) and (6.5.4) respectively.

6.5.2. A SIMPLIFIED EXPRESSION FOR EFFICIENCY

We can find a more useful expression for ΔH appearing in Eq. (6.5.1). This can be obtained by observing that since only energy preserving operations are allowed, we have

$$\text{tr}(\hat{H}_t \rho^0_{\text{ColdHotMW}}) = \text{tr}(\hat{H}_t \rho^1_{\text{ColdHotMW}}), \tag{6.5.9}$$

where $\hat{H}_{\text{ColdHotMW}} = \hat{H}_{\text{Hot}} + \hat{H}_{\text{Cold}} + \hat{H}_{\text{M}} + \hat{H}_{\text{W}}$. Since the Hamiltonian does not contain interaction terms between these systems, the mean energy depends only on the *reduced states* of each system. Mathematically, it means that Eq. (6.5.9) can be written as

$$\text{tr}(\hat{H}_{\text{Hot}} \rho^0_{\text{Hot}}) + \text{tr}(\hat{H}_{\text{Cold}} \rho^0_{\text{Cold}}) + \text{tr}(\hat{H}_{\text{M}} \rho^0_{\text{M}}) + \text{tr}(\hat{H}_{\text{W}} \rho^0_{\text{W}}) = \tag{6.5.10}$$

$$\text{tr}(\hat{H}_{\text{Hot}} \rho^1_{\text{Hot}}) + \text{tr}(\hat{H}_{\text{Cold}} \rho^1_{\text{Cold}}) + \text{tr}(\hat{H}_{\text{M}} \rho^1_{\text{M}}) + \text{tr}(\hat{H}_{\text{W}} \rho^1_{\text{W}}). \tag{6.5.11}$$

Also, note that since $\rho^0_{\text{M}} = \rho^1_{\text{M}}$, therefore $\text{tr}(\hat{H}_{\text{M}} \rho^0_{\text{M}}) = \text{tr}(\hat{H}_{\text{M}} \rho^1_{\text{M}})$. This implies that we have

$$\Delta H = \Delta C + \Delta W, \tag{6.5.12}$$

where

$$\Delta C := \text{tr}\left[\hat{H}_{\text{Cold}} \rho^1_{\text{Cold}}\right] - \text{tr}\left[\hat{H}_{\text{Cold}} \tau^{\beta_c}_{\text{Cold}}\right], \tag{6.5.13}$$

and

$$\Delta W := \text{tr}(\hat{H}_{\text{W}} \rho^1_{\text{W}}) - \text{tr}(\hat{H}_{\text{W}} \rho^0_{\text{W}}). \tag{6.5.14}$$

are changes in average energy of the cold bath and battery. We can thus write Eq. (6.5.1) as

$$\eta = \frac{W_{\text{ext}}}{\Delta W + \Delta C}. \tag{6.5.15}$$

Furthermore, from Eqs. (6.2.5), (6.2.6), (6.2.7) and (6.5.14), we have $\Delta W = (1-\varepsilon) W_{\text{ext}}$, and hence we can write the inverse efficiency as

$$\eta^{-1}(\rho^1_{\text{Cold}}) = 1 - \varepsilon + \frac{\Delta C(\rho^1_{\text{Cold}})}{W_{\text{ext}}(\rho^1_{\text{Cold}})}, \tag{6.5.16}$$

where we have made explicit the ρ^1_{Cold} dependency. We already know from the setting that ρ^0_{Cold} is thermal. If ρ^1_{Cold} is also a thermal state at some temperature β according to the cold bath Hamiltonian $\hat{H}_{\text{Cold}}$, we will sometimes use the shorthand notation $\eta(\beta)$ for $\eta(\rho^1_{\text{Cold}})$ and $\Delta W(\beta)$, $\Delta C(\beta)$ for $\Delta W(\rho^1_{\text{Cold}})$, $\Delta C(\rho^1_{\text{Cold}})$ respectively.

6.6. MAXIMUM EFFICIENCY ACCORDING TO MACROSCOPIC THERMODYNAMICS

In this section, we study the efficiency of the setup detailed in Section 6.2 under the constraints of macroscopic thermodynamics, as described in Section 6.4.1. This implies that the Helmholtz free energy solely dictates whether $\rho^0_{\text{ColdW}} \to \rho^1_{\text{ColdW}}$ is possible.

Box 6.6.1: Maximum efficiency for QHEs according to macroscopic thermodynamics

We find that in both cases of extracting perfect and near perfect work,

(1) The maximum achievable efficiency is the Carnot efficiency.

(2) The Carnot efficiency can be achieved for any cold bath Hamiltonian.

(3) The Carnot efficiency is only achieved when the final state of the cold bath is thermal (according to a different inverse temperature β_f).

(4) The Carnot efficiency is only achieved for quasi-static heat engines.

This section can be summarized as follows: in Section 6.6.1, we first apply the macroscopic law of thermodynamics, namely the fact that Helmholtz free energy is non-increasing, to our heat engine setup. By making use of energy conservation, we can derive the amount of maximum extractable work as shown in Eq. (6.6.5). Next, in Section 6.6.2 we show that when considering the extraction of perfect work, we show the points (1)-(4) as stated above. In Section 6.6.3, we show that points (1)-(4) hold also when considering near perfect work.

The main results can be found in Theorem 6.1 and Lemma 6.6. One may think that the conclusions in Box 6.6.1 are obvious, since it has long been known that the optimal achievable efficiency of a heat engine operating between two thermal baths is the Carnot efficiency, and that this efficiency can only be achieved quasi-statically. The motivations for proving these results here are two-fold. Firstly, this is a rigorous and mathematical proof of optimality, while usually one encounters arguments such as reversibility, or that the heat engine must remain in thermal equilibrium at all times during the working of the heat engine. Secondly, we will find later on at the nano/quantum scale that the Carnot efficiency can be achieved but observation (2) does not hold anymore. For these reasons, it is worthwhile proving that one can actually achieve points (1)-(4) in this setting for any cold bath Hamiltonian according to macroscopic thermodynamics. From a practical point of view, many of the technical results proved here will be needed in the proofs of Section 7.4, where we derive the maximum efficiency for nanoscale quantum systems.

6.6.1. MAXIMUM EXTRACTABLE WORK ACCORDING TO MACROSCOPIC LAW OF THERMODYNAMICS

Our first task is to find an expression for W_{ext} in the macroregime. We do so by solving Eq. (6.4.1) for W_{ext} such that

$$\langle \hat{H}_{\text{ColdMW}} \rangle_{\rho^1_{\text{ColdMW}}} - \frac{1}{\beta_h} S(\rho^1_{\text{ColdMW}}) \leq \langle \hat{H}_{\text{ColdMW}} \rangle_{\rho^0_{\text{ColdMW}}} - \frac{1}{\beta_h} S(\rho^0_{\text{ColdMW}}). \tag{6.6.1}$$

Since the joint Hamiltonian does not contain interaction terms, therefore the mean energy also depends only on the reduced states. Furthermore, entropy is additive under tensor product, therefore one can rewrite Eq. (6.6.1) by expanding its terms,

$$\begin{aligned} &\langle \hat{H}_{\text{Cold}} \rangle_{\rho^1_{\text{Cold}}} + \langle \hat{H}_{\text{M}} \rangle_{\rho^1_{\text{M}}} + \langle \hat{H}_{\text{W}} \rangle_{\rho^1_{\text{W}}} - \frac{1}{\beta_h} \left[S(\rho^1_{\text{Cold}}) + S(\rho^1_{\text{M}}) + S(\rho^1_{\text{W}}) \right] \leq \\ &\langle \hat{H}_{\text{Cold}} \rangle_{\rho^0_{\text{Cold}}} + \langle \hat{H}_{\text{M}} \rangle_{\rho^0_{\text{M}}} + \langle \hat{H}_{\text{W}} \rangle_{\rho^0_{\text{W}}} - \frac{1}{\beta_h} \left[S(\rho^0_{\text{Cold}}) + S(\rho^0_{\text{M}}) + S(\rho^0_{\text{W}}) \right], \end{aligned} \tag{6.6.2}$$

Furthermore, note that $\rho^0_{\text{M}} = \rho^1_{\text{M}}$, and therefore $S(\rho^0_{\text{M}}), \langle \hat{H}_{\text{M}} \rangle_{\rho^0_{\text{M}}}$ are common terms on both sides of Eq. (6.6.2) which can be cancelled out. Furthermore, by our construction of the battery in Eqs. (6.2.5)-(6.2.6), we have that $\langle \hat{H}_{\text{W}} \rangle_{\rho^0_{\text{W}}} = E^{\text{W}}_j$ and $\langle \hat{H}_{\text{W}} \rangle_{\rho^1_{\text{W}}} = (1-\varepsilon)E^{\text{W}}_k + \varepsilon E^{\text{W}}_j$. Thus, Eq. (6.6.2) can be simplified to

$$(1-\varepsilon)W_{\text{ext}} + \langle \hat{H}_{\text{Cold}} \rangle_{\rho^1_{\text{Cold}}} - \frac{1}{\beta_h} S(\rho^1_{\text{Cold}}) \leq \langle \hat{H}_{\text{Cold}} \rangle_{\rho^0_{\text{Cold}}} - \frac{1}{\beta_h} S(\rho^0_{\text{Cold}}) + \frac{1}{\beta_h} \Delta S, \tag{6.6.3}$$

where W_{ext} has been defined in Eq. (6.2.7). Also, noting that $S(\rho^0_{\text{W}}) = 0$, $S(\rho^1_{\text{W}}) = \text{h}_2(\varepsilon)$, therefore $\Delta S = \text{h}_2(\varepsilon)$ and thus $(1-\varepsilon)W_{\text{ext}} \leq F(\rho^0_{\text{Cold}}) - F(\rho^1_{\text{Cold}}) + \frac{1}{\beta_h}\text{h}_2(\varepsilon)$.

We can also express W_{ext} with the *relative entropy* instead, by using Eq. (6.4.5),

$$W_{\text{ext}} \leq (1-\varepsilon)^{-1} \left[F(\rho^0_{\text{Cold}}) - F(\rho^1_{\text{Cold}}) + \frac{1}{\beta_h}\text{h}_2(\varepsilon) \right] \tag{6.6.4}$$

$$= \frac{1}{\beta_h} \left[D(\rho^0_{\text{Cold}} \| \tau^h_{\text{Cold}}) - D(\rho^1_{\text{Cold}} \| \tau^h_{\text{Cold}}) + \text{h}_2(\varepsilon) \right]. \tag{6.6.5}$$

6.6.2. MAXIMUM EFFICIENCY FOR PERFECT WORK IS CARNOT EFFICIENCY

Proof Sketch

In this section, we find the maximum efficiency according to Eq. (6.5.6), for the case of $\varepsilon = 0$ which implies $\text{h}_2(\varepsilon) = 0$. We do this by the following steps:

1. *Evalaute* W_{ext}. According to Eq. (6.6.5), we know that

$$W_{\text{ext}} = F(\rho^0_{\text{Cold}}) - F(\rho^1_{\text{Cold}}) = \frac{1}{\beta_h} \left[D(\rho^0_{\text{Cold}} \| \tau^h_{\text{Cold}}) - D(\rho^1_{\text{Cold}} \| \tau^h_{\text{Cold}}) \right]. \tag{6.6.6}$$

Note that here equality can be achieved because in macroscopic thermodynamics, satisfying the free energy constraint is a necessary and sufficient condition for the

possibility of a state transformation. Note that since by construction the initial and final states of the battery are pure energy eigenstates, namely $\varepsilon = 0$ and therefore

$$W_{\text{ext}} = \Delta W. \tag{6.6.7}$$

2. *Write inverse maximum efficiency as optimization problem.* By substituting the simplified expression for efficiency derived in Eq. (6.5.16) into Eq. (6.5.6), we have
$$\eta_{\max}^{-1} = \inf_{\rho^1_{\text{Cold}}} (\eta^{\text{mac}})^{-1} = 1 + \inf_{\rho^1_{\text{Cold}}} \frac{\Delta C}{W_{\text{ext}}}. \tag{6.6.8}$$

3. *Maximize W_{ext} given a fixed value of ΔC.* In Lemma 6.1, where we show that given a fixed ΔC, the final cold bath state that maximizes W_{ext} is uniquely a thermal state.

4. *Show that 3) implies that efficiency is maximized by a thermal state of the cold bath.* This is proven in Lemma 6.2. Therefore, this implies one only needs to optimize Eq. (6.6.8) over one variable, i.e. β_f, the final temperature of the cold bath.

5. *Show that the efficiency is strictly increasing with β_f.* This is done first by proving several identities, which are summarized in Corollary 6.1. Using these identities, we prove in Lemma 6.4 that the first derivative of efficiency w.r.t. β_f is always positive over the range where $W_{\text{ext}} > 0$. This leads us to conclude, in Theorem 6.1, that maximum efficiency is achieved in the limit $\beta_f \to \beta_c^-$, and evaluating the efficiency at this limit gives us the Carnot efficiency.

Firstly, let us develop a technical Lemma 6.1, which concerns the unique solution towards maximizing W_{ext} for a fixed ΔC. By applying Lemma 6.1, we show in Lemma 6.2 that the maximal efficiency is achieved when ρ^1_{Cold} is a thermal state. The reader can easily find similar proofs in [174].

Lemma 6.1. *Given any Hamiltonian $\hat{H}_{\text{Cold}}$, a corresponding thermal state τ^h_{Cold}, and a fixed initial state ρ^0_{Cold}, consider the maximization over final states ρ^1_{Cold},*

$$\max_{\rho^1_{\text{Cold}}} W_{\text{ext}} \tag{6.6.9}$$

over all block-diagonal states ρ^1_{Cold}, for a fixed value of ΔC. Then the solution for ρ^1_{Cold} is unique: the optimal $\rho^1_{\text{Cold}} = \tau^{\beta'}_{\text{Cold}}$ is the thermal state for some inverse temperature β'.

Proof. Firstly, from Eq. (6.5.13) we see that the constraint ΔC being a constant, is the same as $\text{tr}\left[\hat{H}_{\text{Cold}}\rho^1_{\text{Cold}}\right]$ being a constant. This is because they differ only by a constant term. On the other hand, from Eq. (6.5.14) and (6.6.7), we can see that Eq. (6.6.9) is equal to

$$\max_{\rho^1_{\text{Cold}}} W_{\text{ext}} = \frac{1}{\beta_h}\left[D(\rho^0_{\text{Cold}} \| \tau^h_{\text{Cold}}) - \min_{\rho^1_{\text{Cold}}} D(\rho^1_{\text{Cold}} \| \tau^h_{\text{Cold}})\right]. \tag{6.6.10}$$

Since ρ^1_{Cold} and τ are both diagonal in the energy eigenbasis (ρ^1_{Cold} by the statement in the lemma, and τ by it being a thermal state), one can evaluate the relative entropy by using

Eq. (6.4.3). Denote the eigenvalues of our variable ρ^1_{Cold} to be $\{p_i\}_i$, and the eigenvalues of the thermal state τ to be $\{q_i\}_i$. We can then write the optimization problem as

$$\min_{\{p_i\}} \sum_i p_i(\ln p_i - \ln q_i); \quad \text{subject to } \sum_i p_i E_i = c \quad \text{constant, and } \sum_i p_i = 1,$$

where $q_i = \frac{e^{-\beta E_i}}{Z_\beta}$ and $Z_\beta = \sum_i e^{-\beta E_i}$. We can now employ techniques of Lagrange multipliers to solve this optimization. The constrained Lagrange equation is

$$L(\{p_i\}, \lambda) = \sum_i p_i(\ln p_i - \ln q_i) + \lambda \left(\sum_i E_i p_i - c \right) + \mu \left(\sum_i p_i - 1 \right), \tag{6.6.11}$$

$$\frac{dL}{dp_i} = (\ln p_i - \ln q_i + 1 + \lambda E_i + \mu) = 0, \tag{6.6.12}$$

$$\frac{dL}{d\lambda} = \sum_i E_i p_i - c = 0, \qquad \frac{dL}{d\mu} = \sum_i p_i - 1 = 0. \tag{6.6.13}$$

The normalized solution is

$$p_i = \frac{e^{-\beta' E_i}}{Z_{\beta'}}, \quad Z_{\beta'} = e^{(1+\mu)Z_\beta}, \tag{6.6.14}$$

and p_i are probabilities corresponding to the Boltzmann distribution, according to inverse temperature $\beta' = \beta + \lambda$. Depending on the mean energy constraint c and normalization condition, one can solve for the Lagrange multipliers λ and μ. With this we conclude that the state ρ which maximizes $D(\rho^1_{\text{Cold}} \| \tau)$ is a thermal state, where its temperature is such that the constraint on mean energy is satisfied. □

Lemma 6.2. *Consider the work extraction process described by the state transformation* $\rho^0_{\text{ColdW}} \xrightarrow[\text{CTO}]{} \rho^1_{\text{ColdW}}$, *where* ρ^0_{Cold}, ρ^0_{W} *and* ρ^1_{W} *have been described in Section 6.2. Denote* $\mathscr{H}_{\text{Cold}}$ *as the Hilbert space of the cold bath. Then the maximal efficiency in Eq.* (6.6.8) *is obtained for a final state of the cold bath* ρ^1_{Cold}, *which is thermal:*

$$\eta^{-1}_{\max} = 1 + \inf_{\rho^1_{\text{Cold}} \in S_\tau} \frac{\Delta C}{W_{\text{ext}}}, \tag{6.6.15}$$

where S_τ *the set of all thermal states (for* $\hat{H}_{\text{Cold}}$ *with any temperature* $T > 0$*). Furthermore, all non-thermal states do not achieve the maximum efficiency, i.e.*

$$\eta^{-1}_{\max} < 1 + \frac{\Delta C}{W_{\text{ext}}}\Big|_{\rho^1_{\text{Cold}}} \quad \text{for any } \rho^1_{\text{Cold}} \in S(\mathscr{H}_{\text{Cold}}) \setminus S_\tau. \tag{6.6.16}$$

Proof. First of all, note that without loss of generality we can always consider only block-diagonal final states, since the initial state $\rho^0_{\text{ColdHotMW}}$ is block-diagonal, and that CTOs do not create coherences between energy eigenstates. We begin by substituting Eqs. (6.5.13)

and (6.6.6) into Eq. (6.6.8), and finding

$$\eta_{\max}^{-1} = 1 + \inf_{\rho^1_{\text{Cold}}} \frac{\Delta C}{W_{\text{ext}}} \tag{6.6.17}$$

$$= 1 + \inf_{\rho^1_{\text{Cold}}} \frac{\beta_h \Delta C}{D_1(\tau^c_{\text{Cold}} \| \tau^h_{\text{Cold}}) - D_1(\rho^1_{\text{Cold}} \| \tau^h_{\text{Cold}})} \tag{6.6.18}$$

$$= 1 + \beta_h \left[\sup_{\rho^1_{\text{Cold}}} \frac{D_1(\tau^c_{\text{Cold}} \| \tau^h_{\text{Cold}}) - D_1(\rho^1_{\text{Cold}} \| \tau^h_{\text{Cold}})}{\text{tr}(\hat{H}_{\text{Cold}} \rho^1_{\text{Cold}}) - \text{tr}(\hat{H}_{\text{Cold}} \tau^c_{\text{Cold}})} \right]^{-1}. \tag{6.6.19}$$

In the last line of Eq. (6.6.19), we see that only two terms depend on the maximization variable ρ^1_{Cold}. This means we can perform the maximization in two steps:

$$\sup_{\rho^1_{\text{Cold}}} \frac{D_1(\tau^c_{\text{Cold}} \| \tau^h_{\text{Cold}}) - D_1(\rho^1_{\text{Cold}} \| \tau^h_{\text{Cold}})}{\text{tr}(\hat{H}_{\text{Cold}} \rho^1_{\text{Cold}}) - \text{tr}(\hat{H}_{\text{Cold}} \tau^c_{\text{Cold}})} = \sup_{A>0} \frac{D_1(\tau^c_{\text{Cold}} \| \tau^h_{\text{Cold}}) - B(A)}{A} \tag{6.6.20}$$

where $B(A)$ is the optimal value of a separate minimization problem:

$$B(A) = \inf_{\substack{\rho^1_{\text{Cold}} \in S(\mathcal{H}_{\text{Cold}}) \\ tr(H_{\text{Cold}} \rho^1_{\text{Cold}}) - \text{tr}(\hat{H}_{\text{Cold}} \tau^c_{\text{Cold}}) = A}} D_1(\rho^1_{\text{Cold}} \| \tau^h_{\text{Cold}}) \tag{6.6.21}$$

From Lemma 6.1, we know that the solution of the sub-minimization problem in Eq. (6.6.21) has a unique form, namely $\rho^1_{\text{Cold}} = \tau^f_{\text{Cold}}$ is a thermal state of some temperature β_f. Therefore, Eq. (6.6.20) can be simplified to

$$\sup_{\rho^1_{\text{Cold}}} \frac{D_1(\tau^c_{\text{Cold}} \| \tau^h_{\text{Cold}}) - D_1(\rho^1_{\text{Cold}} \| \tau^h_{\text{Cold}})}{\text{tr}(\hat{H}_{\text{Cold}} \rho^1_{\text{Cold}}) - \text{tr}(\hat{H}_{\text{Cold}} \tau^c_{\text{Cold}})} = \sup_{\beta_f} \frac{D_1(\tau^c_{\text{Cold}} \| \tau^h_{\text{Cold}}) - D_1(\tau^f_{\text{Cold}} \| \tau^h_{\text{Cold}})}{\text{tr}(\hat{H}_{\text{Cold}} \tau^f_{\text{Cold}}) - \text{tr}(\hat{H}_{\text{Cold}} \tau^c_{\text{Cold}})}. \tag{6.6.22}$$

Whats more, for every constant A, the function

$$f(x) = \left(1 + \beta_h \left[\frac{D_1(\tau^c_{\text{Cold}} \| \tau^h_{\text{Cold}}) - x}{A} \right]^{-1} \right)^{-1} \tag{6.6.23}$$

is bijective in $x \in \mathbb{R}$ and thus due to the uniqueness of the sub-minimization problem in Eq. (6.6.21), we conclude that for all non-thermal states ρ^1_{Cold}, the corresponding efficiency will be strictly less than that of Eq. (6.6.19). Thus from Eq. (6.6.22) and (6.6.19) we conclude the lemma. □

We continue to solve the optimization problem in Eq. (6.6.8) by only looking at final states which are thermal (according to some final temperature β_f which we optimize over). In the next Lemma 6.3 and Corollary 6.1, we derive some useful and interesting identities. These identities concern quantities such as the derivatives of mean energy and entropy of the thermal state (with respect to inverse temperature), and relates them to the variance of energy. The reader can find similar proofs in any standard thermodynamic textbook (For example in Sections 6.5, 6. of [175]), but we derive them here for completeness.

Lemma 6.3. *For any cold bath Hamiltonian $\hat{H}_{\text{Cold}}$, consider the thermal state $\tau_\beta = \frac{1}{Z_\beta} e^{-\beta \hat{H}_{\text{Cold}}}$ with inverse temperature β. Define $\langle \hat{H}_{\text{Cold}} \rangle_\beta = \text{tr}(\hat{H}_{\text{Cold}} \tau_\beta)$, and $S(\beta) = -\tau_\beta \ln \tau_\beta$ to be the mean energy and entropy of τ_β. Then the following identities hold:*

$$\frac{d\langle \hat{H}_{\text{Cold}} \rangle_\beta}{d\beta} = -\text{var}(\hat{H}_{\text{Cold}})_\beta, \qquad \frac{dS(\beta)}{d\beta} = -\beta \cdot \text{var}(\hat{H}_{\text{Cold}})_\beta, \tag{6.6.24}$$

where $\text{var}(\hat{H}_{\text{Cold}})_\beta = \langle \hat{H}^2_{\text{Cold}} \rangle_\beta - \langle \hat{H}_{\text{Cold}} \rangle^2_\beta$ is the variance of energy for τ_β.

Proof. Intuitively we know that the expectation value of energy increases as temperature increases (or as β decreases). More precisely, consider the probabilities of τ_β for each energy level of the Hamiltonian $\hat{H}_{\text{Cold}}$, given by $p_i = Z_\beta^{-1} e^{-\beta E_i}$, where $Z_\beta = \sum_i e^{-\beta E_i}$, and

$$\frac{dp_i}{d\beta} = \frac{1}{Z_\beta^2} \left[-E_i e^{-\beta E_i} \cdot Z_\beta - \frac{dZ_\beta}{d\beta} \cdot e^{-\beta E_i} \right] = -p_i E_i - \frac{p_i}{Z_\beta} \frac{dZ_\beta}{d\beta} = -p_i E_i + p_i \langle \hat{H}_{\text{Cold}} \rangle_\beta . \tag{6.6.25}$$

The last equality holds because of the following identity:

$$\frac{-1}{Z} \frac{dZ}{d\beta} = \frac{-1}{Z} \sum_i (-E_i) e^{-\beta E_i} = \sum_i p_i E_i = \langle \hat{H}_{\text{Cold}} \rangle_\beta . \tag{6.6.26}$$

Therefore, we have

$$\frac{d\langle \hat{H}_{\text{Cold}} \rangle_\beta}{d\beta} = \sum_i \frac{d\langle \hat{H}_{\text{Cold}} \rangle_\beta}{dp_i} \frac{dp_i}{d\beta} = \sum_i E_i \cdot \left[-p_i E_i + p_i \langle \hat{H}_{\text{Cold}} \rangle_\beta \right] \tag{6.6.27}$$

$$= -\langle \hat{H}^2_{\text{Cold}} \rangle_\beta + \langle \hat{H}_{\text{Cold}} \rangle^2_\beta = -\text{var}(\hat{H}_{\text{Cold}})_\beta . \tag{6.6.28}$$

On the other hand, similarly, one can prove the second identity by writing down the expression of entropy for the thermal state,

$$S(\beta) = -\sum_i \frac{e^{-\beta E_i}}{Z_\beta} \ln \frac{e^{-\beta E_i}}{Z_\beta} = \sum_i \beta E_i \frac{e^{-\beta E_i}}{Z_\beta} + \ln Z_\beta \sum_i \frac{e^{-\beta E_i}}{Z_\beta} = \beta \langle \hat{H}_{\text{Cold}} \rangle_\beta + \ln Z_\beta . \tag{6.6.29}$$

Therefore, the derivative of $S(\beta)$ w.r.t. β is

$$\frac{dS(\tau_\beta)}{d\beta} = \langle \hat{H}_{\text{Cold}} \rangle_\beta + \beta \frac{d\langle \hat{H}_{\text{Cold}} \rangle_\beta}{d\beta} + \frac{1}{Z_\beta} \frac{dZ_\beta}{d\beta} = \beta \cdot \frac{d\langle \hat{H}_{\text{Cold}} \rangle_\beta}{d\beta} = -\beta \cdot \text{var}(\hat{H}_{\text{Cold}})_\beta . \tag{6.6.30}$$

□

By using Lemma 6.3 in a special case, we obtain the following corollary:

Corollary 6.1. *Given any Hamiltonian $\hat{H}_{\text{Cold}}$, consider the quantities*

$$\Delta C(\beta_f) = \text{tr}(\hat{H}_{\text{Cold}} \tau_{\beta_f}) - \text{tr}(\hat{H}_{\text{Cold}} \tau_{\beta_c}) = \langle \hat{H}_{\text{Cold}} \rangle_{\beta_f} - \langle \hat{H}_{\text{Cold}} \rangle_{\beta_c}, \tag{6.6.31}$$

$$W_{\text{ext}}(\beta_f) = F(\tau_{\beta_c}) - F(\tau_{\beta_f}) = \frac{1}{\beta_h} \left[D(\tau_{\beta_c} \| \tau_{\beta_h}) - D(\tau_{\beta_f} \| \tau_{\beta_h}) \right], \tag{6.6.32}$$

where τ_β corresponds to the thermal state defined by $\hat{H}_{\text{Cold}}$ at inverse temperature β. Then

$$\frac{d\Delta C(\beta_f)}{d\beta_f} = -\text{var}(\hat{H}_{\text{Cold}})_{\beta_f} \tag{6.6.33}$$

$$\frac{dW_{\text{ext}}(\beta_f)}{d\beta_f} = \frac{\beta_h - \beta_f}{\beta_h}\text{var}(\hat{H}_{\text{Cold}})_{\beta_f}. \tag{6.6.34}$$

Proof. For $\Delta C(\beta_f)$, it is straightforward from Lemma 6.3 that

$$\frac{d\Delta C(\beta_f)}{d\beta_f} = \frac{d\langle \hat{H}_{\text{Cold}}\rangle_{\beta_f}}{d\beta_f} = -\text{var}(\hat{H}_{\text{Cold}})_{\beta_f}. \tag{6.6.35}$$

On the other hand, $\Delta W(\beta_f)$ can be simplified by substituting Eq. (6.4.5) into Eq. (6.6.32),

$$W_{\text{ext}}(\beta_f) = F(\tau_{\beta_c}) - F(\tau_{\beta_f}) = \langle \hat{H}_{\text{Cold}}\rangle_{\beta_c} - \langle \hat{H}_{\text{Cold}}\rangle_{\beta_f} - \frac{1}{\beta_h}\left[S(\tau_{\beta_c}) - S(\tau_{\beta_f})\right]. \tag{6.6.36}$$

With this, we can evaluate the derivative by applying Lemma 6.3 for $\frac{d\langle \hat{H}_{\text{Cold}}\rangle_{\beta_f}}{d\beta_f}$, and grouping common factors together:

$$\frac{dW_{\text{ext}}(\beta_f)}{d\beta_f} = -\frac{d\langle \hat{H}_{\text{Cold}}\rangle_{\beta_f}}{d\beta_f} + \frac{1}{\beta_h}\frac{dS(\tau_{\beta_f})}{d\beta_f} = \frac{\beta_h - \beta_f}{\beta_h}\text{var}(\hat{H}_{\text{Cold}})_{\beta_f}.$$

□

In the next step, by using Corollary 6.1, we show that the optimal efficiency is achieved only in the quasi-static limit, i.e. in the limit $\beta_f \to \beta_c^-$.

Lemma 6.4. *Consider the efficiency of a heat engine where $\rho^1_{\text{Cold}} = \tau^f_{\text{Cold}}$,*

$$\eta(\beta_f) = \frac{W_{\text{ext}}(\beta_f)}{\Delta C(\beta_f) + W_{\text{ext}}(\beta_f)}. \tag{6.6.37}$$

Then for all $\beta_f < \beta_c$, $\frac{d\eta(\beta_f)}{d\beta_f} > 0$.

Proof. To prove this, we show that $\frac{d\eta^{-1}}{d\beta_f} < 0$, where $\eta^{-1} = 1 + \frac{\Delta C}{W_{\text{ext}}}$. Evaluating the derivative of η^{-1} w.r.t. β_f, we obtain

$$\frac{d\eta^{-1}}{d\beta_f} = \frac{1}{W_{\text{ext}}^2}\cdot\left[\frac{d\Delta C(\beta_f)}{d\beta_f}W_{\text{ext}} - \frac{dW_{\text{ext}}(\beta_f)}{d\beta_f}\Delta C\right] \tag{6.6.38}$$

$$= \frac{\text{var}(\hat{H}_{\text{Cold}})_{\beta_f}}{W_{\text{ext}}^2}\cdot\left[-W_{\text{ext}} - \frac{\beta_h - \beta_f}{\beta_h}\Delta C\right] \tag{6.6.39}$$

$$= \frac{\text{var}(\hat{H}_{\text{Cold}})_{\beta_f}}{W_{\text{ext}}^2}\cdot\left[\Delta C + \frac{1}{\beta_h}\left[S(\beta_c) - S(\beta_f)\right] - \frac{\beta_h - \beta_f}{\beta_h}\Delta C\right] \tag{6.6.40}$$

$$= \frac{\text{var}(\hat{H}_{\text{Cold}})_{\beta_f}}{W_{\text{ext}}^2}\frac{\beta_f}{\beta_h}\cdot\left[\Delta C - \frac{1}{\beta_f}\left[S(\beta_f) - S(\beta_c)\right]\right]. \tag{6.6.41}$$

The first equality is obtained by invoking the chain rule of differentiation. The second equality is obtained by substituting $\frac{dW_{\text{ext}}}{d\beta_f}'$, $\frac{d\Delta C}{d\beta_f}$, as evaluated earlier in Corollary 6.1. The third equality is obtained by expressing W_{ext} according to Eq. (6.6.36), plus recognizing that $\langle \hat{H}_{\text{Cold}} \rangle_{\tau_{\beta_f}} - \langle \hat{H}_{\text{Cold}} \rangle_{\tau_{\beta_c}} = \Delta C$. The last inequality is obtained, simply by taking out a common term β_f/β_h. We then make the following observations:

1) The factor $\frac{\beta_f}{\beta_h W_{\text{ext}}^2} > 0$,

2) The variance of energy for any positive temperature $\text{var}(\hat{H}_{\text{Cold}})_{\beta_f} > 0$,

3) and the last term $\Delta C - \frac{1}{\beta_f}[S(\beta_f) - S(\beta_c)]$ can be written as $F(\tau_{\beta_f}) - F(\tau_{\beta_c})$, where F is the free energy of a system w.r.t. a bath with inverse temperature β_f. But then, since τ_{β_f} is the thermal state with the same inverse temperature, this means that τ_{β_f} is the *unique* state that minimizes free energy. Therefore, $F(\tau_{\beta_c}) - F(\tau_{\beta_f}) > 0$ for any τ_{β_c}.

□

From Lemma 6.2 and Lemma 6.4, we conclude that the maximization of efficiency for any Hamiltonian $\hat{H}$ happens for a final state which is thermal, and the greater its inverse temperature β_f, the higher efficiency is. With these lemmas we can now prove the main result of this section (Theorem 6.1).

In the next theorem, we evaluate the efficiency at the limit $\beta_f \to \beta_c^-$, and show that it corresponds to the Carnot efficiency.

Theorem 6.1 (Carnot Efficiency)**.** *Consider all heat engines which extract perfect work (see Definition 6.2). Then according to the macroscopic second law of thermodynamics, the maximum achievable efficiency (see Eq.* (6.5.6)*) is the Carnot efficiency*

$$\eta_{\max}^{\text{mac}} = 1 - \frac{\beta_h}{\beta_c}. \tag{6.6.42}$$

It can be obtained for all *cold bath Hamiltonians* $\hat{H}_{\text{Cold}}$*, but* only *for quasi-static heat engines (as defined in Def. 6.1 and Eq.* (6.5.8) *for quasi-static maximum efficiency), where an infinitesimal amount of work is extracted.*

Proof. From Eq. (6.5.6), we have an expression for the optimal efficiency in terms of a maximization over final cold bath states $\rho_{\text{Cold}}^1 \in S(\mathscr{H}_{\text{Cold}})$. By Lemma 6.2, we know that the optimal solution is obtained only for thermal states. Subsequently, by Lemma 6.4, it is shown that when the final cold bath is of temperature β_f, the corresponding efficiency is strictly increasing w.r.t. β_f. Also note that since by definition $W_{\text{ext}} > 0$, this implies that $\beta_f < \beta_c$. Intuitively, this is because heat cannot flow from a cold to hot system without any work input. One can also see this mathematically, by showing that for any $\beta \geq \beta_h$,

$$\frac{dF(\tau_\beta)}{d\beta} = \frac{d}{d\beta}\left[\langle \hat{H}_{\text{Cold}} \rangle_\beta - \frac{1}{\beta_h} S(\beta)\right] = \left(\frac{\beta}{\beta_h} - 1\right) \text{var}(\hat{H}_{\text{Cold}})_\beta \geq 0. \tag{6.6.43}$$

This implies that if $\beta_f \geq \beta_c \geq \beta_h$, then $F(\beta_f) \geq F(\beta_c)$, and according to Eq. (6.6.32) $W_{\text{ext}} \leq 0$. Therefore, the optimal efficiency is achieved only when the $\rho_{\text{Cold}}^1 = \tau_{\text{Cold}}^f$ where β_f

approaches β_c from below. Let $\beta_f = \beta_c - g$, where $g > 0$. Thus we have

$$\eta_{\max}^{-1} = \lim_{g\to 0^+} (\eta^{\text{mac}})^{-1}(\beta_c - g), \quad (\eta^{\text{mac}})^{-1}(\beta_c - g) = 1 + \frac{\Delta C}{W_{\text{ext}}}\Big|_{\rho^1_{\text{Cold}} = \tau_{(\beta_c - g)}}. \tag{6.6.44}$$

Since as $g \to 0^+$, both the numerator and denominator vanish, we can evaluate this limit by first applying L'Hôspital rule, the chain rule for derivatives (for any function F, $\frac{dF}{dg} = -\frac{dF}{d\beta_f}$), and then Corollary 6.1 to obtain

$$\lim_{g\to 0^+} \frac{\Delta C}{W_{\text{ext}}} = \lim_{g\to 0^+} \frac{\frac{d\Delta C}{dg}}{\frac{dW_{\text{ext}}}{dg}} = \lim_{\beta_f \to \beta_c^-} \frac{\frac{d\Delta C}{d\beta_f}}{\frac{dW_{\text{ext}}}{d\beta_f}} = \frac{\beta_h}{\beta_c - \beta_h}.$$

This implies that

$$\eta_{\max}^{-1} = \lim_{g\to 0^+} (\eta^{\text{mac}})^{-1}(\beta_c - g) = 1 + \frac{\beta_h}{\beta_c - \beta_h} = \frac{\beta_c}{\beta_c - \beta_h} \tag{6.6.45}$$

and hence $\eta_{\max} = 1 - \frac{\beta_h}{\beta_c}$. □

6.6.3. MAXIMUM EFFICIENCY FOR NEAR PERFECT WORK IS STILL CARNOT EFFICIENCY

In this section, we show that even while allowing a non-zero failure probability $\varepsilon > 0$ in the near perfect work scenario, the maximum achievable efficiency is still the Carnot efficiency. It is worth noting that this result is also important later, as an upper bound to maximum efficiency in the nanoscopic regime. We first prove it in Lemma 6.5 for the case where the final state of the battery is fixed as in Eq. (6.2.6). Then later, we show in Lemma 6.6 that Carnot is still the maximum, even if we allow a more general final battery state. Before we present the proof, it is useful for the reader to recall the definition of near perfect work (Def. 6.3) and quasi-static heat engines (Def. 6.1).

Lemma 6.5. *Consider all heat engines which extract near perfect work. Then according to the macroscopic second law of thermodyanmics, the maximum efficiency of a heat engine, $\eta_{\max}^{\text{mac}}$ is the Carnot efficiency*

$$\eta_{\max}^{\text{mac}} = \sup_{\rho^1_{\text{Cold}} \in S(\mathcal{H}_{\text{Cold}})} \eta^{\text{mac}}(\rho^1_{\text{Cold}}) = 1 - \frac{\beta_h}{\beta_c}, \tag{6.6.46}$$

and the supremum can only *be achieved for quasi-static heat engines.*

Proof. The ideas in this proof are very similar to that of Section 6.6.2, and the main complication comes from proving that even if we allow $\varepsilon > 0$, as long as $\Delta S / W_{\text{ext}}$ is arbitrarily small, the maximum efficiency cannot surpass the Carnot efficiency.

Let us begin by establishing the relevant quantities for near perfect work extraction. The amount of work extractable from the heat engine, when we have a probability of failure, according to the standard free energy can be obtained by solving Eq. (6.6.6). We thus have that the maximum W_{ext} is

$$W_{\text{ext}} = \beta_h^{-1}(1-\varepsilon)^{-1}\left[D(\tau_{\beta_c} \| \tau_{\beta_h}) - D(\rho^1_{\text{Cold}} \| \tau_{\beta_h}) + \Delta S\right], \tag{6.6.47}$$

where ΔS is defined in Eq. (6.3.1).

Before we continue with the analysis, we will note a trivial consequence of Eq. (6.6.47). Condition 1) in Def 6.3 implies that $(1-\varepsilon)^{-1}$ is upper bounded. The terms in square brackets in Eq. (6.6.47) are also clearly upper bounded for finite β_c, β_h. Hence W_{ext} is bounded from above. ΔS is solely a function of ε and only approaches zero in the limits $\varepsilon \to 0^+$, $\varepsilon \to 1^-$; and $\varepsilon \to 1^-$ is forbidden by 1) in Def 6.3. Thus if 1) and 2) in Def 6.3 are satisfied,

$$\lim_{\varepsilon \to 0^+} \frac{\Delta S}{W_{\text{ext}}} = 0. \tag{6.6.48}$$

In turn, if Eq. (6.6.48) is satisfied, then we have near perfect work by Def. 6.3. Thus Eq. (6.6.48) is satisfied iff we have near perfect work. We will use this result later in the proof.

Extracting a positive amount of near perfect work implies that we can rule out all states ρ^1_{Cold} such that $D(\tau_{\beta_c} \| \tau_{\beta_h}) \leq D(\rho^1_{\text{Cold}} \| \tau_{\beta_h})$ from the analysis. This can be proven by contradiction: if $D(\tau_{\beta_c} \| \tau_{\beta_h}) \leq D(\rho^1_{\text{Cold}} \| \tau_{\beta_h})$, then from Eq. (6.6.47), we have $\beta_h W_{\text{ext}} \leq \Delta S/(1-\varepsilon)$ and together with 2) in Def 6.3 this would imply that $0 < \beta_h(1-\varepsilon) \leq \frac{\Delta S}{W_{\text{ext}}} < p$. If we require this to hold for all $p > 0$, it means ε has to be arbitrarily close to 1. However, since from 1) Def. 6.3 we have $\varepsilon \leq l < 1$, this cannot be satisfied for all $p > 0$, leading to a contradiction.

From Eq. (6.6.8) we have

$$\left(\eta^{\text{mac}}_{\max}\right)^{-1} = 1 - \varepsilon + \inf_{\rho^1_c \in \mathscr{S}} \frac{\Delta C}{W_{\text{ext}}} = (1-\varepsilon) \cdot \left[1 + \frac{\beta_h \Delta C}{D(\tau_{\beta_c} \| \tau_{\beta_h}) - D(\rho^1_{\text{Cold}} \| \tau_{\beta_h}) + \Delta S}\right], \tag{6.6.49}$$

where ΔC and is defined in Eq. (6.5.13).

Firstly, let us show that with a similar analysis as shown in Lemma 6.2, the maximum efficiency occurs when ρ^1_{Cold} is a thermal state. From Eq. (6.6.49), we have

$$\left(\eta^{\text{mac}}_{\max}\right)^{-1} = (1-\varepsilon)\left[1 + \beta_h \inf_{\rho^1_{\text{Cold}} \in \mathscr{S}} \frac{\Delta C}{D(\tau_{\beta_c} \| \tau_{\beta_h}) - D(\rho^1_{\text{Cold}} \| \tau_{\beta_h}) + \Delta S}\right] \tag{6.6.50}$$

$$= (1-\varepsilon)\left[1 + \beta_h \inf_{A>0} \frac{A}{D(\tau_{\beta_c} \| \tau_{\beta_h}) - B(A) + \Delta S}\right] \tag{6.6.51}$$

where

$$B(A) = \inf_{\substack{\rho^1_{\text{Cold}} \in \mathscr{S} \\ tr(\hat{H}_{\text{Cold}} \rho^1_{\text{Cold}}) - \text{tr}(\hat{H}_{\text{Cold}} \tau_{\beta_c}) = A}} D(\rho^1_{\text{Cold}} \| \tau_{\beta_h}). \tag{6.6.52}$$

We can split this minimization problem to Eqs. (6.6.51) and (6.6.52) because $D(\tau_{\beta_c} \| \tau_{\beta_h})$ and ΔS do not depend on the variable ρ^1_{Cold}. Furthermore, when ρ^1_{Cold} is a thermal state of inverse temperature β_f, we have seen in the beginning of the proof in Theorem 6.1 that for $W_{\text{ext}} > 0$, $\beta_f < \beta_c$. This implies that the variable $A = \Delta C = \text{tr}(\hat{H}_{\text{Cold}} \tau_{\beta_f}) - \text{tr}(\hat{H}_{\text{Cold}} \tau_{\beta_c}) > 0$.

By Lemma 6.1, for any fixed $A > 0$ we conclude that the infimum in Eq. (6.6.52) is achieved *uniquely* when ρ^1_{Cold} is a thermal state. Therefore, our optimization problem is simplified to optimization over final temperatures β_f (or $g = \beta_c - \beta_f$),

$$\left(\eta^{\text{mac}}_{\max}\right)^{-1} = (1-\varepsilon) \cdot \left[1 + \beta_h \inf_{\substack{\beta_f \\ \Delta C > 0}} \frac{\Delta C}{D(\tau_{\beta_c} \| \tau_{\beta_h}) - D(\tau_{\beta_f} \| \tau_{\beta_h}) + \Delta S}\right]. \tag{6.6.53}$$

Consider cases of β_f, where $D(\tau_{\beta_c}\|\tau_{\beta_h}) - D(\tau_{\beta_f}\|\tau_{\beta_h})$ is non-vanishing (finite), which are *non quasi-static*. Note that this always corresponds to extracting near perfect work, since when $\varepsilon \to 0^+$, we have $\varepsilon, \Delta S \to 0$ and these contributions dissapear from Eq. (6.6.53). However, by Lemma 6.2 we also know that the infimum over β_f occurs uniquely at the quasi-static limit, when $g \to 0^+$. This means that for all non quasi-static cases, Carnot efficiency cannot be achieved. What remains, is then to consider the quasi-static heat engine. Extracting near perfect work in this case corresponds to requiring that $\lim_{g\to 0^+} \frac{\Delta S}{W_{\text{ext}}} = 0$, where $\varepsilon = \varepsilon(g)$ and $\lim_{g\to 0^+} \varepsilon(g) = 0$. Equivalently, $\lim_{g\to 0^+} \frac{W_{\text{ext}}}{\Delta S} = \infty$. Substituting Eq. (6.6.47) into this relation, we have

$$\lim_{g\to 0^+} (1-\varepsilon(g))^{-1} \left[1 + \frac{D(\tau_{\beta_c}\|\tau_{\beta_h}) - D(\tau_{\beta_f}\|\tau_{\beta_h})}{\Delta S}\right] = \infty \tag{6.6.54}$$

which implies that $\lim_{g\to 0^+} \dfrac{D(\tau_{\beta_c}\|\tau_{\beta_h}) - D(\tau_{\beta_f}\|\tau_{\beta_h})}{\Delta S} = \infty$, or equivalently,

$$\lim_{g\to 0^+} \frac{\Delta S}{D(\tau_{\beta_c}\|\tau_{\beta_h}) - D(\tau_{\beta_f}\|\tau_{\beta_h})} = 0. \tag{6.6.55}$$

Finally, we evaluate the inverse efficiency at the quasi-static limit,

$$\left(\eta_{\max}^{\text{stat,mac}}\right)^{-1} = \lim_{g\to 0^+} (1-\varepsilon(g)) \cdot \left[1 + \beta_h \frac{\Delta C}{D(\tau_{\beta_c}\|\tau_{\beta_h}) - D(\tau_{\beta_f}\|\tau_{\beta_h}) + \Delta S}\right] \tag{6.6.56}$$

$$= 1 + \beta_h \lim_{g\to 0^+} \frac{\Delta C}{D(\tau_{\beta_c}\|\tau_{\beta_h}) - D(\tau_{\beta_f}\|\tau_{\beta_h}) + \Delta S} \tag{6.6.57}$$

$$= 1 + \beta_h \lim_{g\to 0^+} \frac{\Delta C}{\left[D(\tau_{\beta_c}\|\tau_{\beta_h}) - D(\tau_{\beta_f}\|\tau_{\beta_h})\right]} \cdot \left(1 + \frac{\Delta S}{D(\tau_{\beta_c}\|\tau_{\beta_h}) - D(\tau_{\beta_f}\|\tau_{\beta_h})}\right)^{-1} \tag{6.6.58}$$

$$= 1 + \beta_h \lim_{g\to 0^+} \frac{d\Delta C(\tau_{\beta_f})/dg}{dD(\tau_{\beta_f}\|\tau_{\beta_h})/dg} = 1 - \frac{\beta_h}{\beta_h - \beta_c}, \tag{6.6.59}$$

where from Eq. (6.6.58) to (6.6.59), we make use of Eq. (6.6.55): the second term within the limit is simply 1, and the first term depends only on g, which we can obtain Eq. (6.6.59) by invoking the L'Hôspital rule. The last equality in Eq. (6.6.59) then follows directly from the identities we derived for $\frac{dW_{\text{ext}}}{d\beta_f}$ and $\frac{d\Delta C}{d\beta_f}$ in Corollary 6.1,

$$\frac{d\Delta C}{dg} = -\frac{d\Delta C}{d\beta_f} = -\text{var}(\hat{H}_{\text{Cold}})_{\beta_f} \tag{6.6.60}$$

$$\frac{dD(\tau_{\beta_f}\|\tau_{\beta_h})}{dg} = -\frac{dD(\tau_{\beta_f}\|\tau_{\beta_h})}{d\beta_f} = \beta_h \frac{dW_{\text{ext}}}{d\beta_f} = (\beta_h - \beta_f)\text{var}(\hat{H}_{\text{Cold}})_{\beta_f}, \tag{6.6.61}$$

while in the limit $g \to 0,\ \beta_f = \beta_c$.

Finally, we now see that the quasi-static efficiency is

$$\eta_{\max}^{\text{stat,mac}} = \left(\frac{\beta_h - \beta_c - \beta_h}{\beta_h - \beta_c}\right)^{-1} = \frac{\beta_c - \beta_h}{\beta_c} = 1 - \frac{\beta_h}{\beta_c} \tag{6.6.62}$$

which is exactly the Carnot efficiency. □

Later, in Section 7.5.2 we will need Lemma 6.2 to hold in a more general scenario, i.e. instead of the final battery state being $\rho_{\text{W}}^1 = (1-\varepsilon)|E_k\rangle\langle E_k|_{\text{W}} + \varepsilon|E_j\rangle\langle E_j|_{\text{W}}$, we want to allow the final battery state to be any energy block-diagonal state with trace distance ε away from $|E_k\rangle\langle E_k|_{\text{W}}$. Therefore, we prove the next generalized lemma.

Lemma 6.6. *Consider all heat engines which extract near perfect work , but allowing for any final battery state with a trace distance ε to the ideal final pure state $|E_k\rangle\langle E_k|_{\text{W}}$. Then according to the macroscopic second law of thermodynamics, the maximum efficiency of a heat engine, $\eta_{\max}$ is the Carnot efficiency*

$$\eta_{\max}^{\text{mac}} = \sup_{\rho_{\text{Cold}}^1 \in S(\mathscr{H}_{\text{Cold}})} \eta^{\text{mac}}(\rho_{\text{Cold}}^1) = 1 - \frac{\beta_h}{\beta_c}, \tag{6.6.63}$$

and the supremum is only *achieved for quasi-static heat engines.*

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Proof. Firstly, let us note that since the initial state ρ_{ColdW}^0 we start out with is energy block-diagonal, the final state has to also be block-diagonal. Therefore, given the product structure between the cold bath and battery, it is sufficient to consider the case when the final battery state is energy block-diagonal. Next, let us note that any final state ρ_{W}^2 which is energy block-diagonal, and has trace distance ε with $|E_k\rangle\langle E_k|_{\text{W}}$ can be written as,

$$\rho_{\text{W}}^2 = (1-\varepsilon)|E_k\rangle\langle E_k|_{\text{W}} + \varepsilon\rho_{\text{W}}^{\text{junk}}, \text{ where } \rho_{\text{W}}^{\text{junk}} = \sum_i p_i |E_i\rangle\langle E_i|_{\text{W}}, \ \sum_i p_i = 1 \text{ and } p_k = 0. \tag{6.6.64}$$

Next, one can calculate W_{ext} given by the standard free energy condition, i.e.

$$F(\tau_{\beta_c}) + F(\rho_{\text{W}}^0) \geq F(\rho_{\text{Cold}}^1) + F(\rho_{\text{W}}^1). \tag{6.6.65}$$

Using the identity $F(\rho) = \text{tr}(\hat{H}\rho) - \beta^{-1}S(\rho)$, we have that

$$F(\tau_{\beta_c}) + E_j \geq F(\rho_{\text{Cold}}^1) + (1-\varepsilon)E_k + \varepsilon\,\text{tr}(\hat{H}_{\text{W}}\rho_{\text{W}}^{\text{junk}}) - \beta_h^{-1}S(\rho_{\text{W}}^2). \tag{6.6.66}$$

Substituting $W_{\text{ext}} = E_k - E_j$, and rearranging terms, we have

$$(1-\varepsilon)W_{\text{ext}} \leq F(\tau_{\beta_c}) - F(\rho_{\text{Cold}}^1) + \beta_h^{-1}\Delta S - \varepsilon \cdot \left[\text{tr}\left(\hat{H}_{\text{W}}\rho_{\text{W}}^{\text{junk}}\right) - E_j\right]. \tag{6.6.67}$$

Finally, by using the identity (in Eq. (6.4.5)) that $F(\rho) = \beta_h^{-1}[D(\rho\,\|\,\tau_{\beta_h}) - \ln Z_{\beta_h}]$, the maximum amount of extractable work is given by

$$W_{\text{ext}} = (1-\varepsilon)^{-1}\beta_h^{-1} \cdot [D(\tau_{\beta_c}\|\,\tau_{\beta_h}) - D(\rho_{\text{Cold}}^1\|\,\tau_{\beta_h}) + \Delta S - \varepsilon\tilde{E}], \tag{6.6.68}$$

where $\tilde{E} = \text{tr}(\hat{H}_{\text{W}}\rho_{\text{W}}^{\text{junk}}) - E_j$.

Following the steps in Lemma 6.5, in particular the derivations in Eq. (6.6.50) and (6.6.51), we have

$$\left(\eta_{\max}^{\text{mac}}\right)^{-1} = (1-\varepsilon)\cdot\left[1+\beta_h \inf_{\substack{\beta_f \\ \Delta C>0}} \frac{\Delta C}{D(\tau_{\beta_c}\|\tau_{\beta_h}) - D(\tau_{\beta_f}\|\tau_{\beta_h}) + \Delta S - \varepsilon\tilde{E}}\right]. \tag{6.6.69}$$

To show Eq. (6.6.69) gives the Carnot efficiency, we show that 1) for non quasi-static cases where $\beta_f < \beta_c$, Carnot efficiency is not attained, and 2) in the quasi-static limit, Carnot efficiency is attained.

Let us first consider the case of extracting a non-vanishing amount of near perfect work, i.e. for all cases where $\beta_f < \beta_c$. Then near perfect work, by Def. 6.3, corresponds to the limit $\varepsilon \to 0$,

$$\eta^{-1} = \lim_{\varepsilon\to 0}(1-\varepsilon)\cdot\left[1+\beta_h\frac{\Delta C}{D(\tau_{\beta_c}\|\tau_{\beta_h}) - D(\tau_{\beta_f}\|\tau_{\beta_h}) + \Delta S - \varepsilon\tilde{E}}\right] \tag{6.6.70}$$

$$= 1+\beta_h\frac{\Delta C}{D(\tau_{\beta_c}\|\tau_{\beta_h}) - D(\tau_{\beta_f}\|\tau_{\beta_h})}. \tag{6.6.71}$$

In this limit, all terms involving ε vanish, and the inverse efficiency has the same expression as the efficiency for perfect work. We already know from Lemma 6.4 that the infimum over β_f cannot be obtained in this regime, since the inverse efficiency is strictly decreasing with β_f. Therefore, again we are left with analyzing the quasi-static limit for this problem. Following the derivation in Eq. (6.6.58) for the quasi-static limit, we obtain

$$\left(\eta_{\max}^{\text{stat,mac}}\right)^{-1} = 1+\beta_h \lim_{g\to 0^+}\frac{\Delta C}{\left[D(\tau_{\beta_c}\|\tau_{\beta_h}) - D(\tau_{\beta_f}\|\tau_{\beta_h})\right]}\cdot\left(1+\frac{\Delta S - \varepsilon\tilde{E}}{D(\tau_{\beta_c}\|\tau_{\beta_h}) - D(\tau_{\beta_f}\|\tau_{\beta_h})}\right)^{-1}, \tag{6.6.72}$$

where $\varepsilon = \varepsilon(g)$ and note that requiring near perfect work implies that

$$\lim_{g\to 0^+}\frac{\Delta S}{D(\tau_{\beta_c}\|\tau_{\beta_h}) - D(\tau_{\beta_f}\|\tau_{\beta_h})} = 0. \tag{6.6.73}$$

Next, we observe the relationship between ε and ΔS, in the regime where ε is small. Given any $\varepsilon > 0$ denoting the trace distance $d(\rho_{\text{W}}^2, |E_k\rangle\langle E_k|_{\text{W}}) = \varepsilon$, the smallest amount of entropy that can be produced corresponds to $\Delta S = h_2(\varepsilon)$. This is because if we try to distribute the weight ε over more energy eigenvalues, then by majorization the entropy only increases. But we also know that $\varepsilon \le h_2(\varepsilon)$ for small values of ε, in particular over the regime $\varepsilon \in [0, \frac{1}{2}]$. Therefore, we have that in this regime, $\varepsilon \le h_2(\varepsilon) \le \Delta S$ holds. Therefore, we also know that

$$\lim_{g\to 0^+}\frac{\varepsilon\tilde{E}}{D(\tau_{\beta_c}\|\tau_{\beta_h}) - D(\tau_{\beta_f}\|\tau_{\beta_h})} = 0, \tag{6.6.74}$$

where $\varepsilon = \varepsilon(g)$. Plugging Eqns. (6.6.73) and (6.6.74) into Eq. (6.6.72), we have that the quasi-static efficiency is $\eta_{\max}^{\text{stat,mac}} = 1 - \frac{\beta_h}{\beta_c}$. □

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THE EFFICIENCY OF QUANTUM HEAT ENGINES

In the quantum nanoregime, instead of simply the standard free energy that governs transitions for macroscopic thermodynamics, a continuous family of generalized free energies jointly dictate the possibility of a thermodynamical state transition. In this chapter, we show this implies that Carnot's results on efficiency of heat engines needs to be revised. In particular, more information about the bath other than its temperature is required to decide whether maximum (Carnot) efficiency can be achieved. In particular, we derive new fundamental limitations of the efficiency of heat engines that show that the Carnot efficiency can only be achieved under special circumstances, and we derive a new maximum efficiency for others. This renewed understanding of thermodynamics has implications for nanoscale engineering aiming to construct quantum thermal machines. We also show that if one allows for a definition of work that tolerates a non-negligible entropy increase in the battery, then a small scale heat engine can possibly exceed the Carnot efficiency. This can be done without using any additional resources such as coherence or correlations, and furthermore can be achieved by using finite-size quantum heat baths as well. This highlights the importance of choosing a good work quantifier in the quantum nanoregime.

7.1. INTRODUCTION

In this chapter, we consider the generalized second laws applied to the setup of a quantum heat engine which we have seen in Chapter 6. We've seen in Chapter 4 that a whole other family of generalizes second laws jointly determine the possibility of a transition, for nanoscale quantum systems. How does Carnot's result differ in the light of these generalized second laws?

Adopting the setup described with detail in Section 6.2, we turn to the conditions for state transitions of nanoscale quantum systems, as detailed in Section 6.4.2. The reader will see that due to these extra constraints from the generalized free energies, the fundamental limitations on efficiency will differ greatly from the macroscopic observations as derived in Section 6.6. This highlights the difference between a quantum heat engine versus its classical counterpart.

7.1.1. RESULTS AND CONTRIBUTIONS

We show in this chapter that unlike at the macroscopic scale - at which Carnot's fundamental results hold - there is a new fundamental limitation to the maximal efficiency at the nanoscale. Most significantly, this new efficiency depends on the working substance (thermal baths). We find that the Carnot efficiency can be achieved, but only when the thermal baths satisfy certain conditions. Otherwise, a reduced efficiency is obtained, highlighting the significant difference in the performance of heat engines as our devices decrease in size.

No perfect work We show that in the nanoscopic regime, no heat engine can perform perfect work ($\varepsilon = 0$). That is, the efficiency of any such heat engine is zero. More formally, it means that there exists no global energy preserving unitary (see Fig. 6.1) for any $W_{\text{ext}} > 0$.

Efficiency Clearly, however, heat engines *can* be built, prompting the question how this might be possible. We show that for *any* $\varepsilon > 0$, there exists a process such that $W_{\text{ext}} > 0$. Therefore, a heat engine is possible if we ask only for near perfect work. This can even be envisioned in the macroscopic regime, where a heat engine that only extracts work with probability $1 - \varepsilon$, but over many cycles of the engine we do not notice this feature when looking at the average work gained in each run.

To study the efficiency in the nanoscale regime, we have made crucial use of the second laws presented in Chapters 4 and 6. It is apparent from these laws that we might only discover further limitations to the efficiency than we see at the macroscopic scale. Indeed they do arise, as we find that the efficiency no longer depends on just the temperatures of the heat baths. Instead, the explicit structure of the cold bath Hamiltonian $\hat{H}_{\text{Cold}}$ becomes important (a similar argument can be made for the hot bath). Consider a cold bath comprised of n two-level systems everyone with its own energy gap, where n can be arbitrarily large, but finite. Let us denote the spectral gap of the cold bath – the energy gap between its ground state and first excited state – by E_{min}. We can then define the quantity

$$\Omega = \frac{E_{\text{min}}(\beta_{\text{Cold}} - \beta_{\text{Hot}})}{1 + e^{-\beta_{\text{Cold}} E_{\text{min}}}}, \tag{7.1.1}$$

and study the efficiency in the *quasi-static* limit. This means that the final state of the

cold bath is thermal, and its final temperature T_f is higher than T_{Cold} by only a positive infinitesimal amount.

Whenever $\Omega \leq 1$, we show that the maximum and attainable efficiency is indeed the familiar Carnot efficiency, which can be expressed as

$$\eta = \left(1 + \frac{\beta_{\text{Hot}}}{\beta_{\text{Cold}} - \beta_{\text{Hot}}}\right)^{-1}. \tag{7.1.2}$$

However, when $\Omega > 1$, we find a new nanoscale limitation: the efficiency is only

$$\eta = \left(1 + \frac{\beta_{\text{Hot}}}{\beta_{\text{Cold}} - \beta_{\text{Hot}}}\Omega\right)^{-1} \tag{7.1.3}$$

for a quasi-static heat engine. One might hope to obtain a higher efficiency compared to Eq. (7.1.3) by going away from the quasi-static setting, however we also show that such an efficiency is always strictly less than the Carnot efficiency.

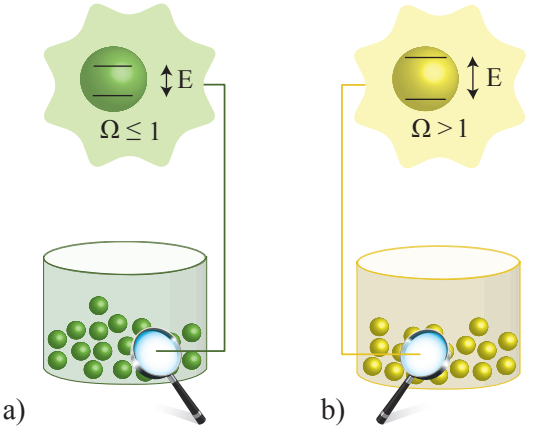

Figure 7.1: **For fixed inverse temperatures β_{Cold}, β_{Hot}, the efficiency of a nanoscale heat engine depends on the structure of the cold bath.** At the nano/quantum scale, Carnot's statement about the universality of heat engines does not hold. We find that the maximum efficiency of a heat engine, *does* depend on the "working fluid". In (a) the energy gaps are small enough to allow the heat engine to achieve Carnot efficiency, i.e., $\Omega \leq 1$. In (b) the efficiency of the heat engine is reduced below the Carnot efficiency because the energy gap of the qubits are above the critical value $\Omega > 1$.

One might question whether the inability to achieve Carnot efficiency always, is a direct consequence of the generalized second laws, or perhaps also either by an overly stringent model of heat engine, or an overly strict characterization of work. However, we show that this is not the case. First of all, since for the macroscopic second law, we recover exactly what Carnot predicted with our setup (in Chapter 6), this implies that our inability to achieve what Carnot predicted according to the macroscopic laws of thermodynamics is not only a consequence of an overly stringent model. Secondly, we even prove our results for a highly generic case (Section 7.5) where the final states of bath, machine and battery may be

correlated. A more generic form of the battery final state can also be allowed. Thirdly, to justify our characterization of work, we also investigate the consequences of allowing for imperfect work, instead of near perfect work. In this case, we show that Carnot efficiency may even be surpassed. This should not come as a surprise, because we are no longer asking for work - energy transfer about which we have (near) perfect information. Our notion of (near) perfect work therefore is one that is necessary, in order to clearly distinct from heat/average energy.

We present results for the full range of possible limits for different types of work extraction, with the corresponding findings about the maximum achievable efficiency for nanoscale heat engines, according to the generalized second laws derived in Chapter 4. We summarize the main results of this chapter in Table 7.1.

Type		**Maximum efficiency**
Perfect work	$\varepsilon = 0$	$W_{\text{ext}} > 0$ is not possible (Lemma 7.2, pg 127).
Near perfect work	$\lim_{\varepsilon\to 0} \frac{\Delta S}{W_{\text{ext}}} = 0$	The Carnot efficiency η_C is the theoretical maximum for all quantum heat engines, and can only be approached uniquely in the quasi-static limit. However, η_C can be approached only if certain conditions on the bath Hamiltonian are met. Otherwise, the maximum attainable efficiency is strictly upper bounded away from η_C. We derive such conditions for an n qubit cold bath (Theorem 7.1, pg 151 and Theorem 7.4, pg 173).
Imperfect work (this paper)	$\lim_{\varepsilon\to 0} \frac{\Delta S}{W_{\text{ext}}} = p,$ $p \in (0,\infty)$	
	∞	Unknown, however examples of exceeding CE can be found (Corollary 7.2, pg 187).

Table 7.1: Different regimes of work corresponding to different limits of the ratio $\lim_{\varepsilon\to 0} \frac{\Delta S}{W_{\text{ext}}}$, and the corresponding findings on the maximum achievable efficiency for a nanoscale quantum heat engine.

7.1.2. CHAPTER OUTLINE

In Section 6.6 of the last chapter, we saw how Carnot's results on heat engines can be re-established in the framework of catalytic thermal operations. We have also seen that the conditions for a particular amount of work extraction are governed by different second laws in ther macroscopic and nanoscopic regime, as detailed in Sections 6.4.1 and 6.4.2. Chapter 6 arrives at the same conclusion as Carnot's result by using the macroscopic second law (for the cases of perfect and near perfect work). However, in this chapter, we will turn expand the full derivation of how these statements change for nanoscale quantum systems.

In particular, Section 7.2 analyzes the case of perfect work. There, we see that for a heat engine operating between two thermal baths, perfect work cannot be extracted.

Sections 7.3-7.5 analyzes the case of near perfect work, where heat contributions are arbitrarily small compared to the amount of energy extracted. Section 7.3 introduces a non-zero failure probability ε for the cases of non-perfect work (for including both near perfect and imperfect work). Building on Section 7.3, in Section 7.4 we analyze the case of near perfect work, where we show how a quantum heat engine may still achieve Carnot efficiency, under certain conditions. Section 7.5 show us how the results of Section 7.4 would still hold, considering an even more general QHE setup which allows final correlations across the bath, battery and machine.

Finally, Sections 7.6 and 7.7 consider the case of imperfect work. Section 7.6 considers the first case of imperfect work as shown in Table 7.1, where the amount of entropy created is still comparable with the amount of extracted energy. In Section 7.7, we show that by using the second type of imperfect work, Carnot efficiency can be surpassed.

7.2. A QHE CANNOT EXTRACT PERFECT WORK

We will first show that with the general setup as described in Section 6.2, no perfect work can ever be extracted. In other words, whenever the failure probability of work extraction $\varepsilon = 0$, then for any value of $W_{\text{ext}} > 0$, and for any final state ρ^1_{Cold}, the transition $|E_j\rangle\langle E_j|_{\text{W}} \otimes \tau^0_{\text{Cold}} \to |E_k\rangle\langle E_k|_{\text{W}} \otimes \rho^1_{\text{Cold}}$ is not possible.

Lemma 7.1. *Consider the Hamiltonian $\hat{H}_{\text{W}}$ given by Eq. (6.2.4), and any two energy levels $E^j_{\text{W}}, E^k_{\text{W}}$ such that $W_{\text{ext}} = E^k_{\text{W}} - E^j_{\text{W}} > 0$. Then for any inverse temperature $\beta_h > 0$, the thermal state $\tau_{\text{W}} = \frac{1}{\text{tr}\left(e^{-\beta_h \hat{H}_{\text{W}}}\right)} e^{-\beta_h \hat{H}_{\text{W}}}$ satisfies*

$$\text{tr}\left[\left(|E_j\rangle\langle E_j|_{\text{W}} - |E_k\rangle\langle E_k|_{\text{W}}\right)\tau_{\text{W}}\right] > 0. \tag{7.2.1}$$

Proof. Follows directly from the definitions. Since $W_{\text{ext}} > 0$, we know that $E^{\text{W}}_j < E^{\text{W}}_k$. Evaluating the quantity above gives $\frac{1}{\text{tr}\left(e^{-\beta_h \hat{H}_{\text{W}}}\right)} \cdot \left(e^{-\beta_h E^{\text{W}}_j} - e^{-\beta_h E^{\text{W}}_k}\right) > 0$. □

Lemma 7.2. *Consider any general quantum state ρ^0_{Cold} of full rank. Then for any ρ^1_{Cold}, the transition from $\rho^0_{\text{Cold}} \otimes \rho^0_{\text{W}} \xrightarrow[\text{CTO}]{} \rho^1_{\text{Cold}} \otimes \rho^1_{\text{W}}$ is not possible if*

$$\text{tr}\left[\left(\Pi_{\rho^0_{\text{W}}} - \Pi_{\rho^1_{\text{W}}}\right)\tau_{\text{W}}\right] > 0, \tag{7.2.2}$$

where Π_ρ is the projector onto the support of state ρ, and τ_{W} is the thermal state of the working body at the initial hot bath temperature.

Proof. One can show this by invoking one of the quantum second laws, in particular for $\alpha = 0$ in Proposition 4.2, which says that if $\rho_{\text{in}} \xrightarrow[\text{CTO}]{} \rho_{\text{out}}$ is possible, then

$$\tilde{D}_0(\rho_{\text{in}} \| \tau) \geq \tilde{D}_0(\rho_{\text{out}} \| \tau), \tag{7.2.3}$$

where τ is the thermal state of the system at bath temperature, and

$$\tilde{D}_0(\rho \| \sigma) = \lim_{\alpha \to 0^+} \frac{1}{\alpha - 1} \ln \text{tr}[\rho^\alpha \sigma^{1-\alpha}] = -\ln \text{tr}[\Pi_\rho \sigma]. \tag{7.2.4}$$

Applying this law with $\rho_{\text{in}} = \rho_{\text{W}}^0 \otimes \rho_{\text{Cold}}^0$ and $\rho_{\text{out}} = \rho_{\text{W}}^1 \otimes \rho_{\text{Cold}}^1$, we arrive at

$$\tilde{D}_0(\rho_{\text{W}}^0 \| \tau_{\text{W}}^h) - \tilde{D}_0(\rho_{\text{W}}^1 \| \tau_{\text{W}}^h) \geq \tilde{D}_0(\rho_{\text{Cold}}^1 \| \tau_{\text{Cold}}^h) - \tilde{D}_0(\rho_{\text{Cold}}^0 \| \tau_{\text{Cold}}^h), \tag{7.2.5}$$

where τ_{Cold}^h and τ_{W}^h are thermal states of the cold bath and battery with inverse temperature β_h respectively. Since ρ_{Cold}^0 has full rank, and since τ_{Cold}^h is normalized, therefore according to Eq. (7.2.4), $\tilde{D}_0(\rho_{\text{Cold}}^0 \| \tau_{\text{Cold}}^h) = 0$. Furthermore, since the $\alpha-$Rényi divergence $\tilde{D}_0$ is non-negative, therefore the r.h.s. of Eq. (7.2.5) is lower bounded by 0. Thus, we have

$$\text{tr}\left[\left(\Pi_{\rho_{\text{W}}^0} - \Pi_{\rho_{\text{W}}^1}\right)\tau_{\text{W}}\right] \leq 0. \tag{7.2.6}$$

Since this is a necessary condition for state transformations, we arrive at the conclusion that: when Eq. (7.2.6) is violated, state transformations are not possible. But from Lemma 7.1, any type of perfect work extraction violates Eq. (7.2.6). Therefore, in this setting, perfect work extraction is always impossible.

□

To summarize, Lemma 7.2 implies that if the initial state of the cold bath is thermal, and therefore of full rank, then any work extraction scheme via CTOs bringing $\rho_{\text{W}}^0 = |E_j\rangle\langle E_j|_{\text{W}}$ to $\rho_{\text{W}}^1 = |E_k\rangle\langle E_k|_{\text{W}}$ where $W_{\text{ext}} = E_k^{\text{W}} - E_j^{\text{W}} > 0$ is not possible. This implies that perfect work, although desirable in principle, is an extremely strict form of work, and cannot be achieved in a generic heat engine setting. Such a phenomena is closely analogous to zero-error data compression: whenever a piece of information is represented by a random variable X over a probability distribution of full rank, then one cannot achieve zero-error in transmission if the data is compressed and transmitted in a message of shorter length [46].

7

7.3. THE EXTRACTION OF NON-PERFECT WORK

Since perfect work cannot be extracted in the setting of a quantum heat engine, we turn to analyze the cases of non-perfect work, i.e. when the probability of failure is $\varepsilon > 0$. Such a regime includes both near perfect work and imperfect work, depending on the value of $\frac{\Delta S}{W_{\text{ext}}}$.

- In Sections 7.3.1 and 7.3.2, we begin by evaluating the expression for efficiency according to the nanoscopic laws of thermodynamics, and comparing it to the expression according to macroscopic law of thermodynamics. The relation between these two efficiencies are summarized in Eq. (7.3.7): the nanoscopic efficiency is always smaller than the macroscopic efficiency. Since the latter attains Carnot efficiency only in the quasi-static limit, it will be possible for the former only to attain Carnot efficiency in the quasi-static limit.

- We analyze the quasi-static regime, focusing on the special case where the cold bath consists of n qubits. Note that the quasi-static limit corresponds to the case of small $g > 0$. In such cases, W_{ext} is infinitesimally small, and therefore ε also has to be arbitrarily small for near perfect work extraction. Moreover, we are also generally interested in cases where the failure probability of work extraction is small. This motivates us to perform Taylor expansion of the analytical expressions for W_{ext} and ΔC w.r.t. g and ε. This is done in Section 7.3.3, and later applied throughout the rest of the chapter.

7.3.1. AN EXPLICIT EXPRESSION FOR W_{ext}

Our first task is to work out an explicit expression for W_{ext} depending on the initial and final states of the cold bath, ε and hot bath (inverse) temperature β_h. Such as expression is found by applying the generalized second laws as detailed in Section 6.4.2.

Lemma 7.3. *Consider the transition*

$$\tau^0_{\text{Cold}} \otimes \rho^0_{\text{W}} \xrightarrow[\text{CTO}]{} \rho^1_{\text{Cold}} \otimes \rho^1_{\text{W}} \quad \text{with} \quad \varepsilon > 0. \tag{7.3.1}$$

where ρ^0_{W} and ρ^1_{W} are defined in Eqs. (6.2.5)*,* (6.2.6) *respectively. Let W_{ext} denote the* maximum *possible value such that Eq.* (7.3.1) *is possible with a thermal bath of inverse temperature β_h. Let $\beta_c > \beta_h$. Then the final state $\rho^1_{\text{Cold}} = \sum_i p'_i |E_i\rangle\langle E_i|_{\text{Cold}}$ is block-diagonal in the energy eigenbasis, and*

$$W_{\text{ext}} = \inf_{\alpha \geq 0} W_\alpha, \tag{7.3.2}$$

$$W_\alpha = \frac{1}{\beta_h(\alpha - 1)} [\ln(A - \varepsilon^\alpha) - \alpha \ln(1 - \varepsilon)], \tag{7.3.3}$$

$$A = \frac{\sum_i p_i^\alpha q_i^{1-\alpha}}{\sum_i p_i'^\alpha q_i^{1-\alpha}}, \tag{7.3.4}$$

where $p_i = \frac{e^{-\beta_c E_i}}{Z_{\beta_C}}$, and $q_i = \frac{e^{-\beta_h E_i}}{Z_{\beta_h}}$. The quantities W_1 and W_∞ are defined by taking the limit $\alpha \to 1, +\infty$ respectively.

Proof. Since both $\tau^0_{\text{Cold}} \otimes \rho^0_{\text{W}}$ and $\rho^1_{\text{Cold}} \otimes \rho^1_{\text{W}}$ are block-diagonal, Eq. (6.4.6) is necessary and sufficient for Eq. (7.3.1) to be satisfied. We can apply the additivity of Rényi divergences, to Eq. (6.4.6):

$$D_\alpha(\rho^0_{\text{W}} \| \tau_{\text{W}}) + D_\alpha(\tau_{\beta_c} \| \tau_{\beta_h}) \geq D_\alpha(\rho^1_{\text{W}} \| \tau_{\text{W}}) + D_\alpha(\rho^1_{\text{Cold}} \| \tau_{\beta_h}), \tag{7.3.5}$$

where τ_{W} is the thermal state with Hamiltonian $\hat{H}_{\text{W}}$ at inverse temperature β_h. We define W_α to be the value of $E^{\text{W}}_k - E^{\text{W}}_j$ that satisfies Eq. (7.3.5) with equality. A straightforward manipulation of these equations gives the expression for W_α. Then $W_{\text{ext}} = \inf_{\alpha \geq 0} W_\alpha$ is the maximum value that satisfies the inequalities Eq. (7.3.5) for all $\alpha \geq 0$. □

We can use this to write down an explicit solution to the maximization problem of evaluating $\eta^{\text{nano}}(\rho^1_{\text{Cold}})$ in Eq. (6.5.2). Using the simplified expression for efficiency in Eq. (6.5.16) and Lemma 7.3, we arrive at

$$\eta^{\text{nano}}(\rho^1_{\text{Cold}}) = \left(1 - \varepsilon + \frac{\Delta C(\rho^1_{\text{Cold}})}{\inf_{\alpha \geq 0} W_\alpha(\rho^1_{\text{Cold}})}\right)^{-1} \tag{7.3.6}$$

where W_α is given by Eqs. (7.3.3), (7.3.4) and recall ΔC can be found in Eq. (6.5.13). From the expression of W_{ext} in Lemma 7.3, we see that the goal of computing the maximum achievable efficiency, $\sup_{\rho^1_{\text{Cold}}} \eta^{\text{nano}}(\rho^1_{\text{Cold}})$ remains a formidable task. In the next section, see will show that we can use the results from Section 6.6, to drastically simplify the problem.

7.3.2. AN UPPER BOUND FOR THE EFFICIENCY

Before moving on to solving the nanoscale efficiency, we will first use the results of Section 6.6.3 to find upper bounds for the efficiency in the nanoscale regime.

Recall how we have observed when comparing Sections 6.4.1 and 6.4.2, that the family of generalized free energies F_α contains the case of F_1, which corresponds to the Helmholtz free energy. Therefore, from Lemma 7.3, it follows that W_1 is simply the maximum amount of extractable work according to the macroscopic law of thermodynamics (as written explicitly in Eq. (6.4.1)). From Eqs. (6.5.4), (6.5.16),

$$\eta^{\mathrm{mac}}(\rho^1_{\mathrm{Cold}}) = \left(1 - \varepsilon + \frac{\Delta C(\rho^1_{\mathrm{Cold}})}{W_1(\rho^1_{\mathrm{Cold}})}\right)^{-1}. \tag{7.3.7}$$

One can now compare Eq. (7.3.7) with Eq. (7.3.6), and note that for any ρ^1_{Cold}, we have $W_1(\rho^1_{\mathrm{Cold}}) \geq \inf_{\alpha\geq 0} W_\alpha(\rho^1_{\mathrm{Cold}})$. Therefore, we conclude that for any ρ^1_{Cold},

$$\eta^{\mathrm{nano}}(\rho^1_{\mathrm{Cold}}) \leq \eta^{\mathrm{mac}}(\rho^1_{\mathrm{Cold}}). \tag{7.3.8}$$

Earlier in Theorem 6.1, we have proven that for the case of near perfect work extraction, $\eta^{\mathrm{mac}}(\rho^1_{\mathrm{Cold}}) \leq \eta_C$. This implies that the same holds for $\eta^{\mathrm{nano}}(\rho^1_{\mathrm{Cold}})$ when extracting near perfect work.

Eq. (7.3.8) in conjunction with Lemma 6.5 has an important consequence. Namely,

$$\sup_{\rho^1_{\mathrm{Cold}}\in S(\mathscr{H}_{\mathrm{Cold}})} \eta^{\mathrm{nano}}(\rho^1_{\mathrm{Cold}}) \tag{7.3.9}$$

$$\begin{cases} \leq 1-\beta_h/\beta_c & \text{if } \rho^1_{\mathrm{Cold}} \text{ that solves the supremum } \textit{is} \text{ that of a quasi-static heat engine,} \\ < 1-\beta_h/\beta_c & \text{if } \rho^1_{\mathrm{Cold}} \text{ that solves the supremum is } \textit{not} \text{ that of a quasi-static heat engine.} \end{cases}$$

This tells us that if we cannot achieve the Carnot efficiency for a quasi-static heat engine, we can then *never* achieve it, and can only achieve a strictly smaller efficiency. Therefore, in order to determine whether a QHE can achieve Carnot efficiency, it suffices to only consider the quasi-static regime.

7.3.3. EVALUATING NON-PERFECT WORK FOR THE QUASI-STATIC HEAT ENGINE

The aim of this section is to provide a calculation for the non-perfect work W_{ext} extractable in quasi-static heat engines, i.e. the case where $\varepsilon, g \ll 1$. This will be done by We first assume, without loss of generality that the cold bath consists of n systems (this is without loss of generality because in particular $n = 1$ can be used). Such an assumption allows us to introduce the parameter n, where ρ^0_{Cold} can be written as

$$\rho^0_{\mathrm{Cold}} = \bigotimes_{i=1}^{n} \tau_{i,\beta_c}, \tag{7.3.10}$$

where τ_{i,β_c} is the thermal state of i-th system Hamiltonian $\hat{H}_{i,\mathrm{c}}$ at inverse temperature β_c. For the simplicity of subsequent proofs, we present them in the special case of identical

systems, i.e. that $\hat{H}_{i,\mathrm{c}} = \hat{H}_{\mathrm{c}}$ for all $1 \leq i \leq n$. This means Eq. (7.3.10) can be reduced to

$$\rho^0_{\mathrm{Cold}} = \tau^{\otimes n}_{\beta_c}. \tag{7.3.11}$$

Furthermore, since we consider quasi-static heat engines, the output state is

$$\rho^1_{\mathrm{Cold}} = \tau^{\otimes n}_{\beta_f}, \tag{7.3.12}$$

with $\beta_f = \beta_c - g$,where $0 < g \ll 1$. Eq. (7.3.11) together with Eq. (7.3.12) allows us to further simplify Eq. (7.3.4) to

$$A = \left(\frac{\sum_i p_i^\alpha q_i^{1-\alpha}}{\sum_i p_i'^\alpha q_i^{1-\alpha}} \right)^n, \tag{7.3.13}$$

where $p_i = \frac{e^{-\beta_c E_i}}{Z_{\beta_c}}$, $p'_i = \frac{e^{-\beta_f E_i}}{Z_{\beta_f}}$, and $q_i = \frac{e^{-\beta_h E_i}}{Z_{\beta_h}}$ are probabilities of thermal states for the Hamiltonian $\hat{H}_{\mathrm{c}}$. The proof is analogous to Lemma 7.3, but now noting that in Eq. (7.3.5) we can replace $D_\alpha(\tau_{\mathrm{Cold}} \| \tau_{\beta_h})$ and $D_\alpha(\rho^1_{\mathrm{Cold}} \| \tau_{\beta_h})$ with $nD_\alpha(\tau_{\beta_c} \| \tau_{\beta_h})$ and $nD_\alpha(\tau_{\beta_f} \| \tau_{\beta_h})$ respectively. This follows from the fact that Rényi divergences are additive.

As mentioned previously, we are interested in the case where both $\varepsilon > 0$ and $g > 0$ are infinitesimally small. With the goal of finding a solution for W_{ext} from Eqs. (7.3.2), (7.3.3), and (7.3.13); we will proceed to find an expansion of W_α for small ε and g.

7

THE EXPANSION OF A FOR A QUASI-STATIC HEAT ENGINE

To simplify our calculations of W_{ext}, especially that of efficiency, it is important to express A in Eq. (7.3.13) in terms of its first order expansion w.r.t. the parameter g. Recall that this parameter $g = \beta_c - \beta_f$ is the difference of inverse temperature between the initial and final state of the cold bath.

Firstly, note that for any integer n, the expression in Eq. (7.3.13) evaluates to $A|_{g=0} = 1$. This is because at $g = 0$, $\beta_f = \beta_c$ and therefore the probabilities p_i, p'_i are identical. To obtain an approximation in the regime $0 < g \ll 1$, we derive

$$\frac{dA}{dg} = -n \left(\sum_i p_i^\alpha q_i^{1-\alpha} \right)^n \left(\sum_i p_i'^\alpha q_i^{1-\alpha} \right)^{-n-1} \left[\sum_i \alpha p_i'^{\alpha-1} q_i^{1-\alpha} \frac{dp'_i}{dg} \right] \tag{7.3.14}$$

$$= -\alpha n A \left(\sum_i p_i'^\alpha q_i^{1-\alpha} \right)^{-1} \left[\sum_i p_i'^\alpha q_i^{1-\alpha} (E_i - \langle \hat{H}_{\mathrm{c}} \rangle_{\beta_f}) \right]. \tag{7.3.15}$$

The first equality holds by noticing that only the probabilities p'_i depend on g, which means only the denominator in Eq. (7.3.13) is differentiated, using the chain rule

$$\frac{dA(\{p'_i\})}{dg} = \sum_i \frac{dA(\{p'_i\})}{dp'_i} \frac{dp'_i}{dg}. \tag{7.3.16}$$

The equality in Eq. (7.3.15) makes use of the fact that $\frac{dp_i'}{dg} = -\frac{dp_i'}{d\beta_f} = p_i'(E_i - \langle \hat{H}_c \rangle_{\beta_f})$ as derived in Eq. (6.6.25). Evaluated at $g = 0$, implies that $p_i' = p_i$, and therefore this gives

$$\left.\frac{dA}{dg}\right|_{g=0} = \alpha n B_\alpha, \quad \text{where} \tag{7.3.17}$$

$$B_\alpha = \frac{1}{\sum_i p_i^\alpha q_i^{1-\alpha}} \sum_i p_i^\alpha q_i^{1-\alpha} \left(\langle \hat{H}_c \rangle_{\beta_c} - E_i\right). \tag{7.3.18}$$

Recall that p_i, q_i are probabilties of the thermal states of $\hat{H}_c$, at inverse temperatures β_c, β_h respectively. With this, we can write the expansion of A with respect to g as

$$A = 1 + \alpha n g B_\alpha + \Theta(g^2). \tag{7.3.19}$$

Later, we need to evaluate the derivative of B_α w.r.t. α. This quantity, at $\alpha = 1$, has a close relation to the change in average energy of the cold bath (per copy), $\frac{\Delta C}{n}$.

Lemma 7.4. *Let*

$$\Delta C'(\beta_c) := \left.\frac{d}{dg} \Delta C(\beta_f)\right|_{g=0}, \tag{7.3.20}$$

where recall $\beta_f = \beta_c - g$. Then

$$B_1' = \left.\frac{dB_\alpha}{d\alpha}\right|_{\alpha=1} = \frac{\beta_c - \beta_h}{n} \Delta C'(\beta_f) = (\beta_c - \beta_h) \cdot \mathrm{var}(\hat{H}_c)_{\beta_c}. \tag{7.3.21}$$

Proof. From the definition of ΔC and using Eqs. (7.4.24), (7.3.10), (7.3.12), we have

$$\frac{\Delta C}{n} = \mathrm{tr}\left[\left(\tau_{\beta_f} - \tau_{\beta_c}\right)\hat{H}_c\right]. \tag{7.3.22}$$

Recalling that $\beta_f = \beta_c - g$ and using Eq. (6.6.35), from Eq. (7.3.22) it follows

$$\frac{1}{n}\Delta C'(\beta_c) = \left.\frac{1}{n}\frac{d\Delta C}{dg}\right|_{g=0} = \left.-\frac{1}{n}\frac{d\Delta C}{d\beta_f}\right|_{\beta_f=\beta_c} = \mathrm{var}(\hat{H}_c)_{\beta_c}. \tag{7.3.23}$$

Now, let us evaluate the partial derivative of B_α w.r.t. α. Denoting $r_i = \frac{p_i}{q_i}$, and invoking the chain rule of derivatives for Eq. (7.3.18), we have

$$\frac{dB_\alpha}{d\alpha} = \left(\sum_i p_i^\alpha q_i^{1-\alpha}\right)^{-2} \left\{ \left[\sum_i q_i r_i^\alpha \ln r_i \cdot \left(\langle \hat{H}_c \rangle_{\beta_c} - E_i\right)\right] \left[\sum_i p_i^\alpha q_i^{1-\alpha}\right] \tag{7.3.24}$$

$$- \left[\sum_i q_i r_i^\alpha \ln r_i\right] \left[\sum_i p_i^\alpha q_i^{1-\alpha} \cdot \left(\langle \hat{H}_c \rangle_{\beta_c} - E_i\right)\right] \Bigg\}. \tag{7.3.25}$$

Substituting $\alpha = 1$ into Eq. (7.3.24), we obtain that $\sum_i p_i^\alpha q_i^{1-\alpha} = 1$. Also, $\sum_i p_i^\alpha q_i^{1-\alpha} \cdot \left(\langle \hat{H}_c \rangle_{\beta_c} - E_i\right) = 0$ while the factor multiplied in front is finite. Therefore, we are left with

$$B_1' = \sum_i p_i \ln r_i \cdot \left(\langle \hat{H}_c \rangle_{\beta_c} - E_i\right) \tag{7.3.26}$$

$$= \sum_i p_i \left[\ln \frac{Z_h}{Z_c} + (\beta_h - \beta_c) E_i\right] \cdot (\langle \hat{H}_c \rangle_{\beta_c} - E_i) \tag{7.3.27}$$

$$= (\beta_c - \beta_h) \cdot \mathrm{var}(\hat{H}_c)_{\beta_c} = \frac{\beta_c - \beta_h}{n} \cdot \Delta C'(\beta_c). \tag{7.3.28}$$

The second equality comes from substituting $r_i = \frac{p_i}{q_i} = e^{(\beta_h - \beta_c)E_i} \cdot Z_h / Z_c$. In the third equality, $\ln \frac{Z_h}{Z_c}$ is brought out of the summation, while the summation yields 0. Subsequently, we invoke $\sum_i p_i E_i (\langle \hat{H}_c \rangle_{\beta_c} - E_i) = \langle \hat{H}_c \rangle_{\beta_c}^2 - \langle \hat{H}_c^2 \rangle_{\beta_c} = -\mathrm{var}(\hat{H}_c)_{\beta_c}$. □

A simple application of Lemma 7.4 is a Taylor expansion for ΔC with respect to the quasi-static parameter g.

Lemma 7.5. *Consider a quasi-static heat engine where the cold bath described by $\hat{H}_{\mathrm{Cold}}$ consists of n identical systems at inverse temperature β_c. Denote the inverse temperature of the hot bath as β_h, and consider the following function*

$$\Delta C := \mathrm{tr}\left(\hat{H}_{\mathrm{Cold}} \tau_{\beta_f}^{\otimes n}\right) - \mathrm{tr}\left(\hat{H}_{\mathrm{Cold}} \tau_{\beta_f}^{\otimes n}\right). \tag{7.3.29}$$

Then in the quasi-static limit, where the cold bath final state is a thermal state of inverse temperature $\beta_f = \beta_c - g$, where $0 < g \ll 1$,

$$\Delta C = \frac{n B_1'}{\beta_c - \beta_h} \cdot g + \Theta(g^2), \tag{7.3.30}$$

where $B_\alpha' = \frac{dB_\alpha}{d\alpha}$ and B_α is defined in Eq. (7.3.18).

Proof. This lemma is directly obtained by Taylor expansion of Eq. (7.3.29), noting two things: 1) that $\Delta C|_{g=0} = 0$, and that 2) when $\rho_{\mathrm{Cold}}^1 = \tau_{\beta_f}$,

$$\left.\frac{d\Delta C}{dg}\right|_{g=0} = \frac{n B_1'}{\beta_c - \beta_h}. \tag{7.3.31}$$

□

THE EXPANSION OF W_α IN THE QUASI-STATIC HEAT ENGINE

We now proceed to derive an expansion of W_α valid for small g, and ε. Note that W_1 is defined through continuity to be the limit of the Rényi divergences at $\alpha \to 1$, and the small ε and g expansion does not hold for $\alpha = 0$, we shall have to examine W_1 and W_0 separately.

(A) For $\varepsilon > 0$, $\alpha \in (0,1) \cup (1,\infty)$

$$W_\alpha = \frac{1}{\beta_h(\alpha-1)}[\ln(A-\varepsilon^\alpha) - \alpha\ln(1-\varepsilon)] \tag{7.3.32}$$

$$= \frac{1}{\beta_h(\alpha-1)}\left[\ln\left(1+\alpha n g B_\alpha + \Theta(g^2) - \varepsilon^\alpha\right) - \alpha\ln(1-\varepsilon)\right] \tag{7.3.33}$$

$$= \frac{1}{\beta_h(\alpha-1)}\left[\alpha n g B_\alpha + \Theta(g^2) - \varepsilon^\alpha + \Theta(\varepsilon^{2\alpha}) + \Theta(g\varepsilon^\alpha) - \alpha\left(-\varepsilon + \Theta\left(\varepsilon^2\right)\right)\right], \tag{7.3.34}$$

$$= \frac{1}{\beta_h(\alpha-1)}\left[\alpha n g B_\alpha - \varepsilon^\alpha + \alpha\varepsilon\right] + \Theta(g^2) + \Theta(\varepsilon^{2\alpha}) + \Theta(g\varepsilon^\alpha) + \Theta(\varepsilon^2). \tag{7.3.35}$$

In the second equality, we have used the expansion of A derived in Eq. (7.3.19). In the third equality, we use the Taylor series for natural logarithm

$$\ln(1+x) = \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k} x^k, \quad |x| < 1, \tag{7.3.36}$$

to expand both of the natural logarithms in Eq. (7.3.32). The order terms of $\Theta(g^3)$, $\Theta(g^4)$, $\Theta(g^2\varepsilon^\alpha)$ vanish because they are of higher order compared with $\Theta(g^2)$ and $\Theta(g\varepsilon^\alpha)$. The last equality occurs because $c\Theta(g(x)) = \Theta(g(x))$ for any $c \in \mathbb{R}\backslash 0$.

(B) For $\varepsilon > 0$, $\alpha = 1$

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Going back to the state transition conditions in Eq. (7.3.5), note that W_1 is the maximum value such that Eq. (7.3.5) holds with equality, when all D_α terms in Eq. (7.3.5) are evaluated at $\alpha \to 1$. Recall that $\lim_{\alpha\to 1} D_\alpha(\rho\|\tau) = D(\rho\|\tau)$ yields the relative entropy. Therefore, one can write an equation for W_1 in a more compact form: W_1 is the value such that

$$n\cdot\left[\langle\hat{H}_c\rangle_{\beta_c} - \frac{1}{\beta_h}S(\beta_c)\right] = n\cdot\left[\langle\hat{H}_c\rangle_{\beta_f} - \frac{1}{\beta_h}S(\beta_f)\right] + (1-\varepsilon)W_1 - \frac{1}{\beta_h}\mathrm{h}_2(\varepsilon), \tag{7.3.37}$$

where $\langle\hat{H}_c\rangle_{\beta_c}$ is the mean energy evaluated at inverse temperature β_{Cold}, $S(\beta_c)$ is the von Neumann entropy of the state τ_{β_c}, and $\mathrm{h}_2(\varepsilon)$ is the binary entropy function. Rearranging Eq. (7.3.37), we get

$$W_1 = \frac{1}{1-\varepsilon}\left[n\langle\hat{H}_c\rangle_{\beta_c} - n\langle\hat{H}_c\rangle_{\beta_f} - n\frac{1}{\beta_h}\left(S(\beta_c) - S(\beta_f)\right) + \frac{1}{\beta_h}\mathrm{h}_2(\varepsilon)\right]. \tag{7.3.38}$$

We can further expand Eq. (7.3.38) using a power law expansion in g and ε for the terms in Eq. (7.3.38), obtaining

$$W_1 = \left[1+\varepsilon+\Theta(\varepsilon^2)\right]\cdot\left[n\frac{d(-\langle\hat{H}_c\rangle_{\beta_f} + \beta_h^{-1}S(\beta_f))}{dg}\Big|_{g=0} g + \Theta(g^2) + \frac{1}{\beta_h}\mathrm{h}_2(\varepsilon)\right]. \tag{7.3.39}$$

To proceed, we recall that $\beta_f = \beta_c - g$ and evaluate the term

$$\left.\frac{d(-\langle \hat{H}_c\rangle_{\beta_f} + \beta_h^{-1} S(\beta_f))}{dg}\right|_{g=0} = \left.\frac{d(\langle \hat{H}_c\rangle_{\beta_f} - \beta_h^{-1} S(\beta_f))}{d\beta_f}\right|_{\beta_f=\beta_c} \tag{7.3.40}$$

$$= -\mathrm{var}(\hat{H}_c)_{\beta_c} + \frac{\beta_c}{\beta_h}\mathrm{var}(\hat{H}_c)_{\beta_c} \tag{7.3.41}$$

$$= \frac{\beta_c - \beta_h}{\beta_h}\mathrm{var}(\hat{H}_c)_{\beta_c}. \tag{7.3.42}$$

This implies that when fully expanded, Eq. (7.3.39) reads as

$$W_1 = ng\frac{\beta_c - \beta_h}{\beta_h}\mathrm{var}(\hat{H}_c)_{\beta_c} + \beta_h^{-1}\mathrm{h}_2(\varepsilon) + \Theta(\varepsilon g) + \Theta(\varepsilon)\mathrm{h}_2(\varepsilon) + \Theta(g\varepsilon^2) + \Theta(\varepsilon^2)\mathrm{h}_2(\varepsilon) \tag{7.3.43}$$

$$+ \Theta(g^2) + \Theta(\varepsilon g^2) + \Theta(\varepsilon^2 g^2) \tag{7.3.44}$$

$$= ng\frac{\beta_c - \beta_h}{\beta_h}\mathrm{var}(\hat{H}_c)_{\beta_c} + \beta_h^{-1}(-\varepsilon\ln\varepsilon + \varepsilon) + \Theta(\varepsilon g) + \Theta(\varepsilon^2\ln\varepsilon) + \Theta(\varepsilon^2) + \Theta(g^2), \tag{7.3.45}$$

where we have used $\mathrm{h}_2(\varepsilon) = -\varepsilon\ln\varepsilon + \Theta(\varepsilon)$, which follows from finding the power-law expansion of the binary entropy.

Although Eq. (7.3.35) is not defined for $\alpha = 1$, we can evaluate it in the limit $\alpha \to 1$ to see if it coincides with the correct expression of W_1 (in Eq. (7.3.45)) at least for the leading order term (found in square brackets of Eq. (7.3.35)). For the leading order term of Eq. (7.3.35), we find

$$\lim_{\alpha\to 1}\frac{1}{\beta_h(\alpha-1)}\left[\alpha ngB_\alpha - \varepsilon^\alpha + \alpha\varepsilon\right] = \beta_h^{-1}\left[ng\lim_{\alpha\to 1}\frac{\alpha B_\alpha}{\alpha-1} - \lim_{\alpha\to 1}\frac{\varepsilon^\alpha - \alpha\varepsilon}{\alpha-1}\right] \tag{7.3.46}$$

$$= \beta_h^{-1}\left[ng\lim_{\alpha\to 1}\frac{\alpha B_\alpha}{\alpha-1} + (-\varepsilon\ln\varepsilon + \varepsilon)\right], \tag{7.3.47}$$

$$= ng\frac{\beta_c - \beta_h}{\beta_h}\mathrm{var}(\hat{H}_c)_{\beta_c} + \beta_h^{-1}(-\varepsilon\ln\varepsilon + \varepsilon). \tag{7.3.48}$$

The last equality holds because

$$\lim_{\alpha\to 1}\frac{\alpha B_\alpha}{\alpha-1} = \lim_{\alpha\to 1}\frac{dB_\alpha}{d\alpha} \tag{7.3.49}$$

$$= (\beta_c - \beta_h)\cdot\mathrm{var}(\hat{H}_c)_{\beta_c}, \tag{7.3.50}$$

where Eq. (7.3.49) is derived from L'Hôspital rule ($B_1 = 0$ follows from the definition, see Eq. (7.3.17)), and Eq. (7.3.50) comes by invoking Lemma 7.4. Thus noting that Eq. (7.3.48) is simply the first two terms in Eq. (7.3.50), we conclude that the small $g > 0$ and $\varepsilon > 0$ expansion of W_α for $\alpha > 0$ can be summarized as

$$W_\alpha = \tag{7.3.51}$$

$$\begin{cases} \frac{1}{\beta_h(\alpha-1)}\left[\alpha ngB_\alpha - \varepsilon^\alpha + \alpha\varepsilon\right] + \Theta(g^2) + \Theta(\varepsilon^{2\alpha}) + \Theta(g\varepsilon^\alpha) + \Theta(\varepsilon^2) & \text{if } \alpha > 0,\ \alpha \neq 1 \\ \lim\limits_{\alpha\to 1^+}\dfrac{1}{\beta_h(\alpha-1)}\left[\alpha ngB_\alpha - \varepsilon^\alpha + \alpha\varepsilon\right] + \Theta(\varepsilon g) + \Theta(\varepsilon^2\ln\varepsilon) + \Theta(\varepsilon^2) + \Theta(g^2) & \text{if } \alpha = 1. \end{cases}$$

(C) For $\alpha = 0$

We will now investigate the $\alpha = 0$ case. This is also particularly important to understand the difference between perfect and non-perfect work, since in Section 7.2, the impossibility of extracting perfect work arises from evaluating the allowed values of W_{ext} under the $\alpha = 0$ constraint. We show that by allowing $\varepsilon > 0$, $W_{\text{ext}} > 0$ is allowed once again. Recall $D_0(p\|q) = \lim_{\alpha\to 0} D_\alpha(p\|q) = \sum_{i:p_i\neq 0} q_i$. Thus from Eq. (7.3.5) we have

$$D_0(\rho_{\text{W}}^0\|\tau_{\text{W}}) - D_0(\rho_{\text{W}}^1\|\tau_{\text{W}}) \geq nD_0(\tau_{\beta_f}\|\tau_{\beta_h}) - nD_0(\tau_{\beta_c}\|\tau_{\beta_h}) = 0. \tag{7.3.52}$$

where the last equality follows from the fact that thermal states have full rank. Whenever $\varepsilon > 0$, this inequality is satisfied for any value of W_{ext} according to Eq. (6.2.5) and (6.2.6). Therefore, taking into account Eqs. (7.3.51) and (7.3.52), for quasi-static heat engines which extract non-perfect work, we only need to solve

$$W_{\text{ext}} = \inf_{\alpha>0} W_\alpha, \tag{7.3.53}$$

where W_α is given by Eq. (7.3.51).

7.4. EFFICIENCY OF A QHE WHEN EXTRACTING NEAR PERFECT WORK

Due to the impossibility result of extracting perfect work, we consider a first relaxation, namely the extraction of near perfect work in the nanoscale setting.

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Box 7.4.1: Maximum efficiency for QHEs according to nanoscopic thermodynamics

For a QHE that extracts near perfect work, we find that

(1) The maximum achievable efficiency is still the Carnot efficiency.

(2) The Carnot efficiency is only achieved when the final cold bath state is thermal (with a different temperature T_f). This is proven in Section 7.3.2.

(3) The Carnot efficiency is only achieved for quasi-static heat engines.

(4) The Carnot efficiency *cannot* be achieved for all cold bath Hamiltonians.This is summarized in Theorem 7.1 (Section 7.4.3). Sections 7.4.1 and 7.4.2 contain technical proofs, that pave the way for deriving this main result.

We give a brief outline the structure for this section:

- In Section 7.4.1, we identify how to choose $\varepsilon(g)$ such that it corresponds to drawing near perfect work in the quasi-static limit. We first begin by observing that any continuous function $\varepsilon(g)$ that vanishes in the limit $g \to 0$ can be characterized with a real-valued parameter $\bar{\kappa}$ that determine how quickly ε goes to zero with respect to g. This is shown in Lemma 7.6. In Lemma 7.7, we show that near perfect work is drawn only if $\bar{\kappa} \in [0, 1]$.

- Lemma 7.7 gives us the analytical expression and minimization range to evaluate W_{ext}, according to Eq. (7.4.6). In Section 7.4.2, we show how one can evaluate this optimization problem, by comparing the stationary points and endpoints of the function $\frac{\alpha B_\alpha}{\alpha-1}$ that gives the leading term in Eq. (7.4.6). Lemma 7.8 proves a technical property of the first derivative of this function. Using it, we prove in Lemma 7.9 that one can always choose $\varepsilon(g)$ with some $\bar{\kappa} < 1$ such that the infimum of $\frac{\alpha B_\alpha}{\alpha-1}$ is obtained at either $\alpha = \bar{\kappa}$ or $\alpha \to \infty$.
- Finally, in Section 7.4.3, we use the results in Section 7.4.2 regarding the evaluation of W_{ext} to find the efficiency in the quasi-static limit.

7.4.1. THE CHOICE OF ε DETERMINES INFIMUM TO EVALUATING W_{ext}

In this section, we will show that the infimum over all $\alpha > 0$ in Eq. (7.3.53) can be simplified to taking the infimum over $\alpha > \bar{\kappa}$ instead for some parameter $\bar{\kappa}$, where $\bar{\kappa}$ determines how quickly ε goes to 0 with respect to the parameter g. We define $\bar{\kappa}$ in Lemma 7.6 and show its existence, for any function of $\varepsilon(g)$ such that $\lim_{g\to 0^+} \varepsilon(g) = 0$.

Lemma 7.6. *For any continuous function $\varepsilon(g) > 0$ satisfying $\lim_{g\to 0^+} \varepsilon(g) = 0$, $\exists\ \bar{\kappa} \in \mathbb{R}_{\geq 0}$ s.t.*

$$\delta(\kappa) = \lim_{g\to 0^+} \frac{\varepsilon^\kappa(g)}{g} = \begin{cases} 0 & \text{if } \kappa > \bar{\kappa} \\ \sigma \geq 0 & \text{if } \kappa = \bar{\kappa} \\ \infty & \text{if } \kappa < \bar{\kappa} \end{cases} \tag{7.4.1}$$

where $\bar{\kappa} = +\infty$ is allowed (that is to say, $\lim_{g\to 0^+} \frac{\varepsilon^\kappa(g)}{g}$ diverges for every $\kappa \in \mathbb{R}_{\geq 0}$) and $\sigma = +\infty$ is also allowed.

Proof. The main idea in this proof is to divide the non-negative real line into an infinite sequence of intervals in an iterative process. We specify the ends of these intervals by constructing a sequence $\{\kappa_i\}_{i=1}^{\infty}$, and evaluating δ at these points. We then prove that according to our construction, there are only two possibilities:
1) κ_i forms a convergent sequence, where the limit $\lim_{n\to\infty} \kappa_n = \bar{\kappa}$, or
2) the ends of these intervals extend to infinity. In this case, $\bar{\kappa} = \infty$.
The way to construct this interval is as follows: in the first round, pick some $\kappa_1 > 0$. The corresponding interval is $[0, \kappa_1]$. Evaluate $\delta(\kappa_1)$. If $\delta(\kappa_1) = \infty$, then proceed to look at the interval $[\kappa_1, \frac{3}{2}\kappa_1]$. Otherwise if $\delta(\kappa_1) < \infty$, choose $\kappa_2 = \frac{\kappa_1}{2}$ and evaluate $\delta(\kappa_2)$. Depending on whether $\delta(\kappa_2)$ goes to infinity, we pick one of the intervals $[0, \kappa_2]$ or $[\kappa_2, \kappa_1]$.

A general expression of choosing κ_n can be written: during the n-th round, define the sets $\mathscr{S}_n^{(0)}, \mathscr{S}_n^{(\infty)}$ such that

$$\mathscr{S}_n^{(0)} = \{\kappa_i | 1 \leq i \leq n \text{ and } \delta(\kappa_i) = 0,\}$$
$$\mathscr{S}_n^{(\infty)} = \{\kappa_i | 1 \leq i \leq n \text{ and } \delta(\kappa_i) = \infty\}.$$

Note that if we find $\delta(\kappa_i) = c \neq 0$ for some finite constant c, then our job is finished, i.e. $\bar{\kappa} = \kappa_i$ (We prove this later). Subsequently, define for $n \geq 1$,

$$\kappa_n^{(0)} = \min_{\kappa\in\mathscr{S}_n^{(0)}} \kappa \qquad \text{and} \qquad \kappa_n^{(\infty)} = \max_{\kappa\in\mathscr{S}_n^{(\infty)}} \kappa.$$

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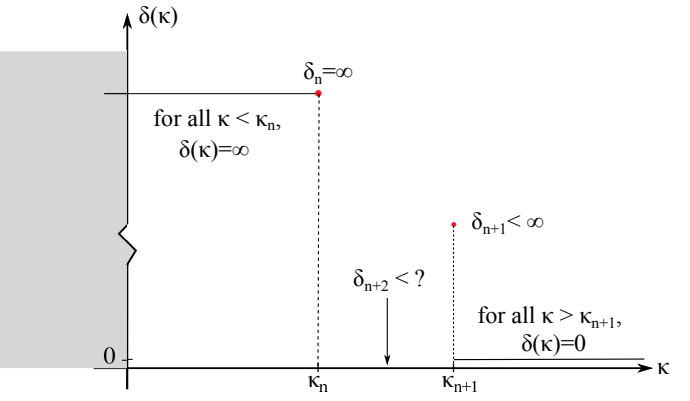

Figure 7.2: Illustration of the scenario where $\delta(\kappa_n) = \infty$ and $\delta(\kappa_{n+1}) < \infty$.

If either sets are empty, we use the convention that the corresponding minimization/maximization equals 0. Once these quantities are defined, we can choose the next interval by evaluating

$$\kappa_{n+1} = \kappa_n^{(\infty)} + \frac{|\kappa_n^{(\infty)} - \kappa_n^{(0)}|}{2}. \tag{7.4.2}$$

In the n-th round, the corresponding interval is $[\kappa_n^{(\infty)}, \kappa_{n+1}]$.

Let us now analyze why we can use this scheme to find $\bar{\kappa}$. Firstly, consider the case where for each κ_i picked, $\delta(\kappa_i) = \infty$. This means that in each round, $\kappa_n^{(\infty)} = \kappa_n$ increases with n (by the iterative scheme), and $\kappa_n^{(0)} = 0$ always stays at zero. Note that this scheme has been constructed in a way such that $\lim_{n\to\infty} \kappa_n = \infty$. Indeed, for all n, by using Eq. (7.4.2),

$$\kappa_{n+1} = \frac{3}{2}\kappa_n = \left(\frac{3}{2}\right)^2 \kappa_{n-1} = \cdots = \left(\frac{3}{2}\right)^n \kappa_1, \tag{7.4.3}$$

which tends to infinity as $n \to \infty$, whenever $\kappa_1 > 0$. Later we will prove a property of the function δ, which combined with this scenario means that $\delta(\kappa) = \infty$ for every $\kappa \geq 0$. Therefore, $\bar{\kappa} = \infty$.

Next, suppose that there exist an n-th round, such that $\delta(\kappa_n) = \infty$ and $\delta(\kappa_{n+1}) < \infty$, as illustrated in Fig 7.2. Note that the function $\delta(\kappa)$ has a peculiar property, i.e. we know that if $\delta(\kappa_n) = \infty$, then for any $\kappa < \kappa_n$,

$$\delta(\kappa) = \lim_{g\to 0^+} \underbrace{\varepsilon^{\kappa-\kappa_n}(g)}_{\to+\infty} \underbrace{\frac{\varepsilon^{\kappa_n}(g)}{g}}_{\to\infty} = +\infty. \tag{7.4.4}$$

On the other hand, if $\delta(\kappa_{n+1}) = 0$, then we know that for any $\kappa > \kappa_{n+1}$,

$$\delta(\kappa) = \lim_{g\to 0^+} \underbrace{\varepsilon^{\kappa-\kappa_{n+1}}(g)}_{\to 0} \underbrace{\frac{\varepsilon^{\kappa_{n+1}}(g)}{g}}_{\to 0} = 0. \tag{7.4.5}$$

Moreover, if $\delta(\kappa_j) = c \neq 0$ for some positive, finite c, then following the same arguments, one can easily see that for all $\kappa < \kappa_j$, $\delta(\kappa) = \infty$ and for $\kappa > \kappa_j$, $\delta(\kappa) = 0$. In this case we find that $\bar{\kappa} = \kappa_j$. These observations are illustrated in Figure 7.2 for clarity.

One can now evaluate κ_{n+2} (which is the midpoint of κ_n and κ_{n+1}) and its corresponding value of $\delta(\kappa_{n+2})$. From this point on, in each iteration we either find $\bar{\kappa}$ exactly (whenever the function δ when evaluated produces a finite, non-zero number), or the length of the next interval gets halved, and goes to zero in the limit of $n \to \infty$. This, by Eq. (7.4.2), also implies that $\lim_{n\to\infty} \kappa_n^{(\infty)} = \lim_{n\to\infty} \kappa_n^{(0)}$. We also know the following:

1) for all $\kappa < \kappa_n^{(\infty)}$, $\delta(\kappa) = \infty$,

2) for all $\kappa > \kappa_n^{(0)}$, $\delta(\kappa) = 0$.

Therefore, $\bar{\kappa}$ exists and $\bar{\kappa} = \lim_{n\to\infty} \kappa_n^{(\infty)} = \lim_{n\to\infty} \kappa_n^{(0)}$. By this we conclude the proof. □

To provide some intuition about how $\bar{\kappa}$ compares the rate of convergence $\varepsilon, g \to 0$, let us look at the following examples:

1) Consider $\varepsilon_1(g) = \exp(-1/g)$. Then $\bar{\kappa} = 0$ with $\sigma = \infty$.

2) Consider $\varepsilon_2(g) = g \ln g$. Then $\bar{\kappa} = 1$ with $\sigma = \infty$.

3) Consider $\varepsilon_3(g) = c \cdot g^{1/k}$ for $k > 0$. Then $\bar{\kappa} = k$ with $\sigma = c$.

NEAR PERFECT WORK CORRESPONDS TO $\bar{\kappa} \in [0, 1]$

In the next lemma, we consider the scenario of near perfect work, given in Def. 6.3, and show that this imposes a finite range of values $\bar{\kappa}$ should take. Given a particular $\bar{\kappa}$, we also show that the minimization of Eq. (7.3.53) changes with $\bar{\kappa}$.

Lemma 7.7. *Consider any $\varepsilon(g) \in (0, 1]$ as a continuous function of g, where $g > 0$. If $\lim_{g\to 0^+} \varepsilon(g) = 0$ and $\lim_{g\to 0^+} \frac{\Delta S}{W_{\text{ext}}} = 0$, then the following holds:*

1. *The quantity $\bar{\kappa}$ (defined in Lemma 7.6) is within the interval $\bar{\kappa} \in [0, 1]$, where the limit $\lim_{g\to 0^+} \frac{\varepsilon \ln \varepsilon}{g} = 0$ has to hold if $\bar{\kappa} = 1$.*

2. *The amount of extractable work can be written as*

$$W_{\text{ext}} = g \cdot \left[\inf_{\alpha \geq \bar{\kappa}} \frac{n\alpha B_\alpha}{\alpha - 1} + f(g) \right], \tag{7.4.6}$$

where $\lim_{g\to 0^+} f(g) = 0$ and $\inf_{\alpha\geq\bar{\kappa}}$ can be exchanged for $\inf_{\alpha>\bar{\kappa}}$ if $\bar{\kappa} = 0$.

Proof. Firstly, Eq. (7.3.51) simplifies our expression for W_{ext}: $W_{\text{ext}} = \inf_{\alpha\geq 0} W_\alpha$, where

$$\beta_h W_\alpha = \begin{cases} g\tilde{W}_\alpha + \Theta(g^2) + \Theta(\varepsilon^{2\alpha}) + \Theta(g\varepsilon^\alpha) + \Theta(\varepsilon^2) & \text{if } \alpha \in (0,1) \cup (1,\infty) \\ g\tilde{W}_1 + \Theta(\varepsilon g) + \Theta(\varepsilon^2 \ln \varepsilon) + \Theta(\varepsilon^2) + \Theta(g^2) & \text{if } \alpha = 1, \end{cases} \tag{7.4.7}$$

and

$$\tilde{W}_\alpha := \frac{1}{\alpha - 1} \left(\alpha n B_\alpha + \alpha \frac{\varepsilon}{g} - \frac{\varepsilon^\alpha}{g} \right), \tag{7.4.8}$$

and for $\alpha = 1$

$$\tilde{W}_1 = \left(\lim_{\alpha\to 1} \frac{\alpha n B_\alpha}{\alpha - 1}\right) + \frac{\varepsilon}{g} - \frac{\varepsilon}{g}\ln(\varepsilon). \tag{7.4.9}$$

From now on, the order terms in Eq. (7.4.7) can be neglected, since it can be checked that all of them are of higher order compared to the terms we grouped in $\tilde{W}_\alpha$, in the limit of vanishing g. Even then, we note that due to the complicated form of W_{ext}, it is not straightforward to begin our proof with the assumption $\lim_{g\to 0^+} \frac{\Delta S}{W_{\text{ext}}} = 0$.

Instead, we begin by noting that given a function $\varepsilon(g)$ that satisfies the conditions of the above lemma, then one can invoke Lemma 7.6, and therefore there exists a $\bar{\kappa} \in \mathbb{R}_{\geq 0}$ such that Eq. (7.4.1) holds. We then, for all possible $\kappa \in \mathbb{R}_{\geq 0}$, evaluate all $\tilde{W}_\alpha$ to take the infimum and obtain W_{ext}. Given W_{ext}, we then evaluate the quantity $\lim_{g\to 0^+} \frac{\Delta S}{W_{\text{ext}}} = 0$.

The value of $\bar{\kappa}$ determines how the limits of quantities like $\frac{\varepsilon}{g}, \frac{\varepsilon^\alpha}{g}$ behave. Therefore, we need to split the analysis into three different regimes: $\bar{\kappa} \in [0,1)$, $\bar{\kappa} = 1$, $\bar{\kappa} \in (1,\infty)$.

1) For $\bar{\kappa} \in [0,1)$

For this case, we know the following limits:

A. $\lim_{g\to 0^+} \frac{\varepsilon}{g} = 0$.

B. For $\alpha < \bar{\kappa}$, $\lim_{g\to 0^+} \frac{\varepsilon^\alpha}{g} = \infty$.

C. For $\alpha = \bar{\kappa}$, $\lim_{g\to 0^+} \frac{\varepsilon^\alpha}{g} = \sigma \geq 0$.

D. For $\alpha > \bar{\kappa}$, $\lim_{g\to 0^+} \frac{\varepsilon^\alpha}{g} = 0$.

E. Note that $\exists\, k_1 > \bar{\kappa}$ such that $1 - k_1 > 0$. Thus $\lim_{g\to 0^+} \frac{\varepsilon}{g}\ln\varepsilon = \lim_{g\to 0^+} \frac{\varepsilon^{k_1}}{g}\varepsilon^{1-k_1}\ln\varepsilon = 0$.

Therefore, by using Eq. (7.4.8) and (7.4.9) (for $\alpha = 1$ separately) we have

$$\tilde{W}_\alpha = \begin{cases} +\infty & \text{if } \alpha \in [0,\bar{\kappa}) \\ \dfrac{\alpha n B_\alpha}{\alpha - 1} + \sigma + \Theta\left(\dfrac{\varepsilon}{g}\right) & \text{if } \alpha = \bar{\kappa} \\ \dfrac{\alpha n B_\alpha}{\alpha - 1} + \Theta\left(\dfrac{\varepsilon^\alpha}{g}\right) & \text{if } \alpha \in (\bar{\kappa},1) \\ \dfrac{\alpha n B_\alpha}{\alpha - 1} + \Theta\left(\dfrac{\varepsilon}{g}\right) & \text{if } \alpha \in (1,\infty) \\ \lim\limits_{\alpha\to 1} \dfrac{\alpha n B_\alpha}{\alpha - 1} + \Theta\left(\dfrac{\varepsilon\ln\varepsilon}{g}\right) & \text{if } \alpha = 1, \end{cases} \tag{7.4.10}$$

where the expression in Eq.(7.4.10) has been written as a leading order term, plus higher order terms that vanish in the limit $g \to 0$.

Therefore, we conclude that for $\bar{\kappa} \in [0,1)$ and any $\sigma \geq 0$, due to continuity in α of $\frac{\alpha n B_\alpha}{\alpha - 1}$,

$$\beta_h W_{\text{ext}} = \inf_{\alpha>0} W_\alpha = g \cdot \left[\inf_{\alpha\geq\bar{\kappa}} \frac{\alpha n B_\alpha}{\alpha - 1} + \Theta\big(f(g)\big)\right], \tag{7.4.11}$$

where f satisfies $\lim_{g\to 0^+} f(g) = 0$ in the expression of Eq. (7.4.10), Both functions vanish as g tends to zero. Note that if $\bar{\kappa} = 0$, then $\inf_{\alpha\geq\bar{\kappa}}$ can be exchanged for $\inf_{\alpha>\bar{\kappa}}$ since in Eq. (7.3.53) the point $\alpha = 0$ was already excluded.

We can now calculate $\lim_{g\to 0^+}\frac{\Delta S}{W_{\text{ext}}}$ for $\bar{\kappa}\in[0,1)$ and any $\sigma\geq 0$:

$$\begin{aligned}\lim_{g\to 0^+}\frac{\Delta S}{W_{\text{ext}}} &= \lim_{g\to 0^+}\frac{-\varepsilon\ln\varepsilon-(1-\varepsilon)\ln(1-\varepsilon)}{\left(\inf_{\alpha\geq\bar{\kappa}}\frac{\alpha nB_\alpha}{\alpha-1}\right)g} \\ &= \lim_{g\to 0^+}\frac{1}{\inf_{\alpha\geq\bar{\kappa}}\frac{\alpha nB_\alpha}{\alpha-1}}\left(\underbrace{-\frac{\varepsilon\ln\varepsilon}{g}}_{\to 0\text{ (Item E)}}-\underbrace{\frac{\varepsilon+\Theta(\varepsilon^2)}{g}}_{\to 0\text{ (Item A)}}\right)=0,\end{aligned} \tag{7.4.12}$$

where we have assumed that

$$\inf_{\alpha\geq\bar{\kappa}}\frac{\alpha nB_\alpha}{\alpha-1}>0. \tag{7.4.13}$$

As we will see later (see Eq. (7.4.30)), Eq. (7.4.13) holds if $\bar{\kappa}>0$. However,

$$\frac{\alpha nB_\alpha}{\alpha-1}=0, \tag{7.4.14}$$

if $\alpha=0$ and we need to use Eq. (7.4.10) for the case $\alpha\in(\bar{\kappa},1)$ for $\bar{\kappa}=0$. From which we conclude that

$$\beta_h W_{\text{ext}}=\inf_{\alpha>0}W_\alpha\geq\varepsilon^{1/2}=\Theta(f(g)), \tag{7.4.15}$$

thus we have

$$\lim_{g\to 0^+}\frac{\Delta S}{W_{\text{ext}}}\leq\lim_{g\to 0^+}\frac{-\varepsilon\ln\varepsilon-(1-\varepsilon)\ln(1-\varepsilon)}{\varepsilon^{1/2}/g}=\lim_{g\to 0^+}g(-\varepsilon^{1/2}\ln\varepsilon-\varepsilon^{1/2})=0. \tag{7.4.16}$$

thus from Eqs. (7.4.14), (7.4.15), and (7.4.16), we conclude that Eq. Eqs. (7.4.11) and (7.4.12) are still valid when $\bar{\kappa}=0$. To summarize, so far we have proven that whenever $\bar{\kappa}\in[0,1)$, Eq. (7.4.6) holds for some $f(g)$ which vanishes as g tends to zero, and furthermore $\lim_{g\to 0^+}\frac{\Delta S}{W_{\text{ext}}}=0$.

2) For $\bar{\kappa}\in(1,\infty)$

In this regime, like the previous analysis, we can list out the following limits:

A. $\lim_{g\to 0^+}\frac{\varepsilon}{g}=0$.

B. By definition of $\bar{\kappa}$, for $\alpha<1$, $\lim_{g\to 0^+}\frac{\varepsilon^\alpha}{g}=\infty$.

C. $\lim_{g\to 0^+}\frac{\varepsilon\ln\varepsilon}{g}=\infty$ since both $\frac{\varepsilon}{g}$ and $\ln\varepsilon$ goes to infinity as $g\to 0$.

Therefore, by using Eq. (7.4.8) and (7.4.9) (for $\alpha=1$ separately) we have

$$\tilde{W}_\alpha=\begin{cases}\frac{1}{g}\cdot\frac{1}{1-\alpha}\left[\varepsilon^\alpha+\Theta(\varepsilon)+\Theta(g)\right] & \text{if } \alpha\in[0,1)\\ \frac{1}{g}\cdot\left[-\varepsilon\ln\varepsilon+\Theta(\varepsilon)+\Theta(g)\right] & \text{if } \alpha=1\\ \frac{1}{g}\cdot\frac{1}{\alpha-1}\left[\alpha\varepsilon+\Theta(\varepsilon^\alpha)+\Theta(g)\right] & \text{if } \alpha\in(1,\infty).\end{cases} \tag{7.4.17}$$

Note that for all of these expressions in Eq. (7.4.17), $\tilde{W}_\alpha \to \infty$. Next we want to calculate W_{ext}, which is the infimum of W_α, taken over all $\alpha \geq 0$. Note that in the limit of vanishing g, ε also goes to zero. Therefore in Eq. (7.4.17), the equation of $\tilde{W}_\alpha$ which vanishes most quickly in the limit $g \to 0$ happens when $\alpha \in (1,\infty)$. Therefore, we conclude that for $\bar{\kappa} \in (1,\infty)$ and any $\sigma \geq 0$,

$$\beta_h W_{\text{ext}} = \inf_{\alpha \geq 1} W_\alpha = g \cdot \left[\inf_{\alpha \geq 1} \frac{\alpha}{\alpha - 1} \frac{\varepsilon}{g} + \Theta\big(f(g)\big) \right] = \varepsilon + g \cdot \Theta\big(f(g)\big) \tag{7.4.18}$$

We can now calculate $\lim_{g \to 0^+} \frac{\Delta S}{W}$ for $\bar{\kappa} \in (1,\infty)$ and any $\sigma \geq 0$:

$$\lim_{g \to 0^+} \frac{\Delta S}{W} = \lim_{g \to 0^+} \frac{-\varepsilon \ln \varepsilon - (1-\varepsilon)\ln(1-\varepsilon)}{\varepsilon} = \lim_{g \to 0^+} \underbrace{-\frac{\varepsilon \ln \varepsilon}{\varepsilon}}_{\to \infty} - \underbrace{\frac{\varepsilon + \Theta(\varepsilon^2)}{\varepsilon}}_{\to 1} = +\infty. \tag{7.4.19}$$

From this, we note that the whole regime of $\bar{\kappa} \in (1,\infty)$ does not contain any cases corresponding to our condition of interest: $\lim_{g \to 0^+} \frac{\Delta S}{W_{\text{ext}}} = 0$ never holds.

3) For $\bar{\kappa} = 1$

Similar to the first two cases, we again list out the relevant limits:
A. $\lim_{g \to 0^+} \frac{\varepsilon}{g} = \sigma$ for some $\sigma \geq 0$.
B. For $\alpha < 1$, $\lim_{g \to 0^+} \frac{\varepsilon^\alpha}{g} = \infty$.
C. For $\alpha > 1$, $\lim_{g \to 0^+} \frac{\varepsilon^\alpha}{g} = 0$.
Therefore, by using Eq. (7.4.8) and (7.4.9) (for $\alpha = 1$ separately) we have

$$\tilde{W}_\alpha = \begin{cases} \frac{1}{g} \cdot \frac{1}{1-\alpha} \left[\varepsilon^\alpha + \Theta(\varepsilon) + \Theta(g) \right] & \text{if } \alpha \in [0,1) \\ \frac{1}{g} \cdot \left[-\varepsilon \ln \varepsilon + \Theta(\varepsilon) + \Theta(g) \right] & \text{if } \alpha = 1 \ \ \&\& \ \ \sigma > 0 \\ n \lim_{\alpha \to 1} \frac{\alpha B_\alpha}{\alpha - 1} - \frac{\varepsilon \ln \varepsilon}{g} \geq n \lim_{\alpha \to 1} \frac{\alpha B_\alpha}{\alpha - 1} & \text{if } \alpha = 1 \ \ \&\& \ \ \sigma = 0 \\ \frac{1}{\alpha - 1} \left[\alpha n B_\alpha + \alpha\sigma - \Theta\left(\frac{\varepsilon^\alpha}{g}\right) \right] & \text{if } \alpha \in (1,\infty). \end{cases} \tag{7.4.20}$$

Note that for $\alpha \in [0,1)$ and the case $\alpha = 1$ && $\sigma > 0$, $\tilde{W}_\alpha$ tends to infinity, while for the other cases $\tilde{W}_\alpha$ is finite.

Therefore, we can conclude that for $\bar{\kappa} = 1$,

$$\beta_h W_{\text{ext}} = g \cdot \left[\left(\inf_{\alpha \geq 1} \frac{\alpha}{\alpha - 1} (n B_\alpha + \sigma) \right) + \Theta\big(f(g)\big) \right], \tag{7.4.21}$$

where $f(g) = \frac{\varepsilon^\alpha}{g}$ vanishes as g tends to zero.

Now, we evaluate the limit $\lim_{g \to 0^+} \frac{\Delta S}{W}$ for $\bar{\kappa} = 1$ and any $\sigma \geq 0$:

$$\lim_{g \to 0^+} \frac{\Delta S}{W} = \lim_{g \to 0^+} \frac{-\varepsilon \ln \varepsilon - (1-\varepsilon)\ln(1-\varepsilon)}{\left(\inf_{\alpha \geq 1} \frac{1}{\alpha - 1} (\alpha n F_\alpha + \alpha\sigma) \right) g} = \lim_{g \to 0^+} \frac{-\varepsilon \ln \varepsilon}{c \cdot g} - \underbrace{\frac{\varepsilon + \Theta(\varepsilon^2)}{c \cdot g}}_{\to 0}. \tag{7.4.22}$$

This limit of interest can be zero if and only if $\lim_{g\to 0^+} \frac{\varepsilon \ln \varepsilon}{g} = 0$.

We have calculated the limits $\lim_{g\to 0^+} \Delta S/W_{\text{ext}}$ to leading order in g for all functions $\varepsilon(g) > 0$ satisfying $\lim_{g\to 0^+} \varepsilon = 0$. These are found in Eqs. (7.4.12), (7.4.19), and (7.4.22). We have found that $\lim_{g\to 0^+} \Delta S/W_{\text{ext}} = 0$ occurs only in two cases:
i) $\bar{\kappa} \in [0,1)$, and
ii) $\bar{\kappa} = 1$ and $\lim_{g\to 0^+} \frac{\varepsilon \ln \varepsilon}{g} = 0$.
The amount of work, W_{ext} is found in Eq. (7.4.11) and (7.4.21) respectively. Indeed, they take the form of Eq. (7.4.6), for different functions $f(g)$. With this, we conclude the proof of the lemma. □

Therefore, since we have analyzed in Lemma 7.7 the full range of $\bar{\kappa} \in \mathbb{R}_{\geq 0}$, we summarize the possible functions of $\varepsilon(g)$ into the following Table 7.2, for any continuous function $\varepsilon(g)$ such that $\lim_{g\to 0} \varepsilon(g) = 0$.

	$\lim_{g\to 0} \frac{\Delta S}{W_{\text{ext}}}$	Characterization
Near perfect work	0	$\bar{\kappa} \in [0,1)$
		$\bar{\kappa} = 1 \ \wedge \ \lim_{g\to 0} \frac{\varepsilon \ln \frac{1}{\varepsilon}}{g} = 0$
Imperfect work	$p > 0$	$\bar{\kappa} = 1 \ \wedge \ \lim_{g\to 0} \frac{\varepsilon \ln \frac{1}{\varepsilon}}{g} = p', \ 0 < p' < \infty$
	∞	$\bar{\kappa} = 1 \ \wedge \ \sigma = p'' > 0$ $\left(\text{This implies that } \lim_{g\to 0} \frac{\varepsilon \ln \frac{1}{\varepsilon}}{g} = \infty\right)$
		$\bar{\kappa} \in (1,\infty)$

Table 7.2: Each choice of a continuous function ε such that $\lim_{g\to 0} \varepsilon = 0$, can lead to different regimes of $\frac{\Delta S}{W_{\text{ext}}}$ in the quasi-static limit, depending on the values of $\bar{\kappa}, \sigma$ and $\lim_{g\to 0} \frac{-\varepsilon \ln \varepsilon}{g}$. Recall Lemma 7.6 for definitions of $\bar{\kappa}$ and σ.

7.4.2. SOLVING THE INFIMUM FOR W_{ext}

We have seen in Lemma 7.7 that the function $\frac{\alpha B_\alpha}{\alpha - 1}$ corresponds to the largest order term in W_{ext} w.r.t. small g (quasi-static heat engine). Our next objective is to find the infimum of $\frac{\alpha B_\alpha}{\alpha - 1}$ over $\alpha \in [\bar{\kappa}, \infty]$ appearing in Eq. (7.4.6). Such an infimum is is not easy to evaluate for an arbitrary Hamiltonian, but whenever the cold bath consists simply of multiple identical qubits, we show that the derivative $\frac{d}{d\alpha} \frac{\alpha B_\alpha}{\alpha - 1}$ has some nice properties. Roughly speaking, this derivative does not have many roots, which in turn means that $\frac{\alpha B_\alpha}{\alpha - 1}$ does not have many

turning points. We have used this to prove in Lemma 7.9 that the infimum is either obtained at $\alpha = \bar{\kappa}$ or $\alpha \to \infty$.

Let us begin by noting that the derivative of $\frac{\alpha B_\alpha}{\alpha-1}$ w.r.t. α is given by

$$\frac{d}{d\alpha}\frac{\alpha B_\alpha}{\alpha-1} = \frac{B_\alpha}{\alpha-1} + \alpha\frac{B'_\alpha}{\alpha-1} - \frac{\alpha B_\alpha}{(\alpha-1)^2} = \frac{B'_\alpha}{(\alpha-1)^2}\left[\alpha(\alpha-1) - \frac{B_\alpha}{B'_\alpha}\right] = \frac{B'_\alpha}{(\alpha-1)^2}G(\alpha), \tag{7.4.23}$$

where $G(\alpha) := \alpha(\alpha-1) - \frac{B_\alpha}{B'_\alpha}$. To simplify our analysis, in addition to the generic assumptions (A.1)-(A.4) elaborated in Section 6.2, **from now onwards we make the following additional assumption about the cold bath Hamiltonian**:

(A.5) The Hamiltonian is taken to be of n qubits:

$$\hat{H}_{\text{Cold}} = \sum_{k=1}^{n} \mathbb{1}^{\otimes(k-1)} \otimes \hat{H}_{\text{c},k} \otimes \mathbb{1}^{\otimes(n-k)}, \quad \text{where} \quad \hat{H}_{\text{c},k} = E_k|E_k\rangle\langle E_k|, \tag{7.4.24}$$

and $E_k > 0$ is the energy gap of the k-th qubit. We present the subsequent proofs first for the case of identical qubits, more precisely, the case where $E_k = E$ for all $1 \le k \le n$. Later on, we show in Theorem 7.1 that the main result can be extended to non-identical qubits.

With this assumption, we evaluate the quantities B_α, B'_α, and $\frac{d}{d\alpha}\frac{B_\alpha}{B'_\alpha}$. Firstly, we start by evaluating B_α as defined by Eq. (7.3.18) to obtain a simple expression:

$$B_\alpha = E\cdot\frac{e^{-\beta_c E}}{1+e^{-\beta_c E}} - E\cdot\frac{e^{-\alpha\beta_c E}e^{-(1-\alpha)\beta_h E}}{1+e^{-\alpha\beta_c E}e^{-(1-\alpha)\beta_h E}} \tag{7.4.25}$$

$$= E\cdot\frac{1}{1+e^{\beta_c E}} - E\cdot\frac{e^{\alpha\beta_h E}}{e^{\alpha\beta_h E}+e^{(\beta_h+\alpha\beta_c)E}} \tag{7.4.26}$$

$$= \frac{E}{1+e^{\beta_c E}}\cdot\left[1 - \frac{e^{\alpha\beta_h E}\left(1+e^{\beta_c E}\right)}{e^{\alpha\beta_h E}+e^{(\beta_h+\alpha\beta_c)E}}\right] \tag{7.4.27}$$

$$= \frac{E}{1+e^{\beta_c E}}\cdot\frac{e^{(\beta_h+\alpha\beta_c)E} - e^{(\beta_c+\alpha\beta_h)E}}{e^{\alpha\beta_h E}+e^{(\beta_h+\alpha\beta_c)E}} \tag{7.4.28}$$

$$= \frac{E}{1+e^{\beta_c E}}\cdot e^{(\beta_h+\alpha\beta_c)E}\cdot\frac{1-e^{-(\alpha-1)(\beta_c-\beta_h)E}}{e^{\alpha\beta_h E}+e^{(\beta_h+\alpha\beta_c)E}}. \tag{7.4.29}$$

We note that Eq. (7.4.28) is zero only if $\alpha = 1$, and thus for $\alpha \neq 1$, $\alpha B_\alpha/(\alpha-1) \neq 0$. Furthermore, note that by examining the third term in Eq. (7.4.29), we see that $B_\alpha < 0$ if $\alpha - 1 \le 0$, while $B_\alpha > 0$ if $\alpha - 1 \ge 0$. Therefore, we can conclude that

$$\frac{\alpha B_\alpha}{\alpha-1} > 0 \quad \forall\ \alpha > 0. \tag{7.4.30}$$

We also derive the first derivative of B_α w.r.t. α for the special case of qubits:

$$B'_\alpha = \frac{dB_\alpha}{d\alpha} = \frac{E^2(\beta_c-\beta_h)}{\left[e^{\alpha\beta_h E}+e^{(\beta_h+\alpha\beta_c)E}\right]^2}\cdot e^{(\beta_h+\alpha\beta_c+\alpha\beta_h)E}. \tag{7.4.31}$$

Note that since $\beta_c > \beta_h$ by our construction, therefore whenever $E > 0$, then $B'_\alpha > 0$ always holds. By further algebraic manipulation, we compute the first derivative of the function

$$\frac{d}{d\alpha}\frac{B_\alpha}{B'_\alpha} = \frac{\cosh[w(\beta_c,\beta_h,\alpha)E]}{\cosh(\beta_c E/2)}, \tag{7.4.32}$$

where $w(\beta_c,\beta_h,\alpha) = (\beta_c-\beta_h)\alpha + \beta_h - \frac{\beta_c}{2}$.

We have written Eq. (7.4.23) in this form, since for the special case of qubits, namely Eq. (7.4.31), $B'_\alpha > 0$ is always true. Therefore, looking at the function $G(\alpha)$ whether it is positive or negative) will tell us whether $\frac{\alpha B_\alpha}{\alpha-1}$ (and therefore W_α) is increasing or decreasing in a particular interval.

In Lemma 7.8, we identify the conditions on the energy spacing E such that several different properties of $G(\alpha)$ hold.

Lemma 7.8. *Consider* $G(\alpha) = \alpha(\alpha-1) - \frac{B_\alpha}{B'_\alpha}$, *where* B_α, B'_α *is defined in Eq.* (7.4.28) *and* (7.4.31). *Then the following holds:*
1) If $E(\beta_c-\beta_h)\tanh(\beta_c E/2) > 2$,

$$\exists\, 0<\tau<1 \text{ s.t.} \quad G(\alpha) < 0 \quad \forall \alpha \in (\tau,1)\cup(1,\infty) \tag{7.4.33}$$

2) If $E(\beta_c-\beta_h)\tanh(\beta_c E/2) < 2$,

$$\begin{aligned} \exists\, \underline{\alpha} > 1 \text{ s.t.} \qquad & G(\alpha) > 0 \quad \forall \alpha \in (0,1)\cup(1,\underline{\alpha}) \\ & G(\alpha) < 0 \quad \forall \alpha \in (\underline{\alpha},\infty). \end{aligned} \tag{7.4.34}$$

3) If $E(\beta_c-\beta_h)\tanh(\beta_c E/2) = 2$,

$$\begin{aligned} & G(\alpha) > 0 \quad \forall \alpha \in (0,1) \\ & G(\alpha) < 0 \quad \forall \alpha \in (1,\infty). \end{aligned} \tag{7.4.35}$$

Proof. First we note that since $B_1 = 0$, therefore $G(1) = 0$. Let us also compute the derivative of $G(\alpha)$ w.r.t. α:

$$G'(\alpha) = 2\alpha - 1 - \frac{\cosh\left((-\beta_c/2 + \beta_h + (\beta_c-\beta_h)\alpha)E\right)}{\cosh(\beta_c E/2)}. \tag{7.4.36}$$

Before we continue, there are several properties of the function $G'(\alpha)$ which we shall make use of. Firstly, note that $G'(1) = 0$, in other words, G' has a root at $\alpha = 1$. Also, $G'(\infty) = -\infty$ for any value of $E > 0$, $\beta_h > 0$, $\beta_c > \beta_h$[1]. Also, since $2\alpha - 1$ is linear (and hence both convex and concave), while the $-\cosh$ function is strictly concave[2] , therefore the function $G'(\alpha)$ is *strictly concave*. This implies that the second derivative $G''(\alpha) = \frac{d^2G(\alpha)}{d\alpha^2}$ is strictly decreasing w.r.t. α.

These properties of $G'(\alpha)$ indicate that we can fully analyze the function by considering 3 different cases:

[1] This is due to the fact that 2α increases linearly w.r.t. α, while the cosh term increases exponentially.

[2] To be more precise; due to the concavity of $f(x) = -a\cosh(b+xc)$ for $a > 0$. This follows from the strict concavity of the cosh function, the invariancy of strict concavity under an affine transformation and the invariancy of strict concavity under multiplication by a positive constant.

1. $G''(1) < 0$. This is when G' has two roots at $\alpha = \{\underline{a}, 1\}$, wherewhere $\underline{a} \in (-\infty, 1)$.
2. $G''(1) > 0$. This is when G' has two roots at $\alpha = \{1, \overline{a}\}$, where $\overline{a} \in (1, \infty)$.
3. $G''(1) = 0$. This is when G' has a single root at $\alpha = 1$.

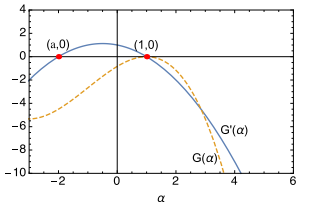

Figure 7.3: $G''(1) < 0$.

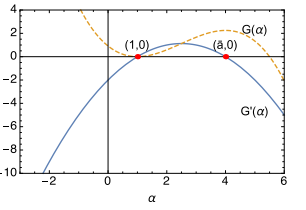

Figure 7.4: $G''(1) > 0$.

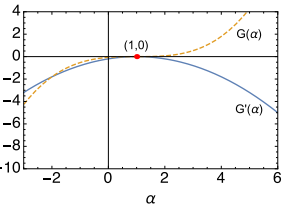

Figure 7.5: $G''(1) = 0$.

We shall now consider these cases one by one. Suppose that

$$G''(1) = G''(\alpha)\Big|_{\alpha=1} = 2 - (\beta_c - \beta_h)E \tanh\left(\frac{\beta_c E}{2}\right) < 0, \tag{7.4.37}$$

then $G''(\alpha) < 0$ for all $\alpha \in (1, \infty)$. Note that Eq. (7.4.37) corresponds to the first condition in the lemma stated above.

This information about the second derivative $G''(\alpha)$ now allows us to conclude the following about $G(\alpha)$:

1. If for all $\alpha \in (1, \infty)$, $G''(\alpha) < 0$, then we know that $G'(\alpha) < 0$ holds for all $\alpha \in (1, \infty)$ too. Furthermore, this implies that $G(\alpha)$ is monotonically decreasing in the interval $(1, \infty)$ and therefore, $G(\alpha) < 0$ for all $\alpha \in (1, \infty)$.
2. $G''(1) < 0$ also implies that there exists an interval $(\tau, 1)$ such that $G'(1) > 0$ (See Fig. 7.3). And since $G(1) = 0$, this implies that within the interval $(\tau, 1)$, $G(\alpha) < 0$.

With this, we prove the first statement of the lemma.

Let us now analyze the second case, where $G''(1) > 0$. This implies that $G'(\alpha) > 0$ at least for some interval $\alpha \in (1, \overline{a})$, then $G'(\alpha)$ changes sign exactly once at $\alpha = \overline{a}$, and goes to $-\infty$. (Refer to Fig. 7.4). Also, recall that in the limit of $\alpha \to \infty$, G also goes to $-\infty$. Therefore, we conclude that there exists some $\overline{\alpha}$ such that

$$G(\alpha) \begin{cases} > 0 & \alpha \in (1, \overline{\alpha}) \\ < 0 & \alpha \in (\overline{\alpha}, \infty) \end{cases} \tag{7.4.38}$$

With this, we prove the second statement of the lemma.

Finally, we look at the case where $G''(1) = 0$, and make the following observations:

1. Since the function $G'(\alpha)$ is concave, and since $G''(1) = 0$ implies that $\alpha = 1$ is an extremum point for the function $G'(\alpha)$, we know that it must also be the global maximum. Therefore, we know that for any $\alpha \neq 1, G'(\alpha) < 0$.

2. Since for the interval $\alpha \in (-\infty, 1), G'(\alpha) < 0$ and we know that $G(1) = 0$, therefore we can deduce that for any $\alpha \in (-\infty, 1)$, $G(\alpha) > 0$.

3. Since for the interval $\alpha \in (1, \infty), G'(\alpha) < 0$ and we know that $G(1) = 0$, therefore we can deduce that for any $\alpha \in (1, \infty)$, $G(\alpha) < 0$.

With this, we prove the final statement of the lemma, and complete our proof. □

To summarize, in Lemma 7.8 we have identified conditions involving the energy gap of $\hat{H}_c$, and the temperatures β_h, β_c. Depending on whether these conditions are satisfied, we can describe the positivity/negativity of $G(\alpha)$ for different regimes of α. Comparing these different scenarios, we prove in Lemma 7.9 that for a quasi-static heat engine, the minimum of $\inf_{\alpha \geq \bar{\kappa}} \frac{\alpha B_\alpha}{\alpha - 1}$ is obtained only either at $\alpha = \bar{\kappa}$ or $\alpha = \infty$.

Lemma 7.9. *There exists some $0 \leq \nu < 1$ such that $\forall\ \kappa$ satisfying $\nu < \kappa < 1$, the following infimum is obtained at one of two points*

$$\inf_{\alpha \geq \kappa} \frac{\alpha B_\alpha}{\alpha - 1} = \inf\left\{ \lim_{\alpha \to \kappa} \frac{\alpha B_\alpha}{\alpha - 1}, \lim_{\alpha \to \infty} \frac{\alpha B_\alpha}{\alpha - 1} \right\} < \lim_{\alpha \to \kappa'} \frac{\alpha B_\alpha}{\alpha - 1}, \qquad \forall \kappa' \in (\kappa, \infty), \tag{7.4.39}$$

where B_α is defined in Eq. (7.4.28). Furthermore, if $E(\beta_c - \beta_h)\tanh(\beta_c E/2) \leq 2$, then we can set $\nu = 0$.

Proof. 1. If

$$\frac{d}{d\alpha}\frac{\alpha B_\alpha}{\alpha - 1} \begin{cases} > 0\ \forall\ \alpha \in (0,1) \cup (1, \overline{\alpha}) \text{ for some } \overline{\alpha} \geq 1 \\ < 0\ \forall\ \alpha \in (\overline{\alpha}, \infty). \end{cases} \tag{7.4.40}$$

then $\forall\ \kappa \in (0,1)$,

$$\inf_{\alpha \geq \kappa} \frac{\alpha B_\alpha}{\alpha - 1} = \inf\left\{ \lim_{\alpha \to \kappa} \frac{\alpha B_\alpha}{\alpha - 1}, \lim_{\alpha \to \infty} \frac{\alpha B_\alpha}{\alpha - 1} \right\} < \lim_{\alpha \to \kappa'} \frac{\alpha B_\alpha}{\alpha - 1}, \qquad \forall \kappa' \in (\kappa, \infty). \tag{7.4.41}$$

Recall from Eq. (7.4.23) that

$$\frac{d}{d\alpha}\frac{\alpha B_\alpha}{\alpha - 1} = \frac{B'_\alpha}{(\alpha - 1)^2} G(\alpha), \tag{7.4.42}$$

where $B'_\alpha > 0$, and we have derived some properties of $G(\alpha)$ in Lemma 7.8. In this proof, we apply Lemma 7.8 directly to consider the three scenarios detailed in Lemma 7.8.

First, consider the first statement of Lemma 7.8. If $E(\beta_c - \beta_h)\tanh(\beta_c E/2) > 2$, then $\exists$ $0 < t < 1$ s.t.

$$\frac{d}{d\alpha}\frac{\alpha B_\alpha}{\alpha - 1} < 0, \qquad \forall \alpha \in (t, 1) \cup (1, \infty), \tag{7.4.43}$$

then by continuity of $\frac{\alpha B_\alpha}{\alpha - 1}$ in α, we conclude that $\forall \kappa$ satisfying $t < \kappa < 1$,

$$\inf_{\alpha \geq \kappa} \frac{\alpha B_\alpha}{\alpha - 1} = \lim_{\alpha \to \infty} \frac{\alpha B_\alpha}{\alpha - 1} < \lim_{\alpha \to \kappa'} \frac{\alpha B_\alpha}{\alpha - 1}, \qquad \forall\ \kappa' \in (\kappa, \infty). \tag{7.4.44}$$

Next, let us consider the second and third statements of Lemma 7.8 jointly, where $E(\beta_c - \beta_h)\tanh(\beta_c E/2) \leq 2$. Note that both statements proved in Lemma 7.8 (namely, Eq. (7.4.34) and (7.4.35)) can be rewritten as the fact that there exists $\overline{\alpha} \geq 1$ s.t.

$$\frac{d}{d\alpha}\frac{\alpha B_\alpha}{\alpha - 1} \begin{cases} > 0 & \text{for } \alpha \in (0,1) \cup (1, \overline{\alpha}) \\ < 0 & \text{for } \alpha \in (\overline{\alpha}, \infty). \end{cases} \tag{7.4.45}$$

In fact, the third statement is simply a special case of the second, where $\overline{\alpha} = 1$. If Eq. (7.4.45) holds, then $\forall\ \kappa \in (0,1)$,

$$\inf_{\alpha \geq \kappa} \frac{\alpha B_\alpha}{\alpha - 1} = \inf\left\{ \lim_{\alpha \to \kappa} \frac{\alpha B_\alpha}{\alpha - 1}, \lim_{\alpha \to \infty} \frac{\alpha B_\alpha}{\alpha - 1} \right\} < \lim_{\alpha \to \beta} \frac{\alpha B_\alpha}{\alpha - 1} \quad \forall\ \beta \in (\kappa, \infty). \tag{7.4.46}$$

By setting $\tau = 0$, we see that the statement of Lemma 7.9 is achieved.

Therefore, since we have analyzed all three cases stated in Lemma 7.8, we conclude that there always exists $\nu \in [0,1)$ such that Eq. (7.4.39) will always be satisfied $\forall\ \kappa \in (\nu, 1)$. □

7.4.3. EVALUATING THE MAXIMUM EFFICIENCY FOR NANOSCALE QHES

In this section, we derive the efficiency of quasi-static heat engines in the nano /quantum regime. We first need to define the quantity

$$\Omega := \min_{i \in \{1,\ldots,n\}} \frac{E_i(\beta_c - \beta_h)}{1 + e^{-\beta_c E_i}}, \tag{7.4.47}$$

where recall that E_i is the energy gap of the cold bath qubits, as described in Eq. (7.4.24). Before stating the maximum efficiency, we will derive the efficiency as a function of $\bar{\kappa}$ defined in Lemma 7.6 (recall that this parameter is determined by the choice of ε). For simplicity, we will still consider the special case where $E_i = E$ for all i in Lemma 7.10. Lemma 7.10 shows us that under the condition of extracting near perfect work, one can choose ε (and therefore $\bar{\kappa}$) such that a certain maximum efficiency value is achieved. The closer $\bar{\kappa}$ is to unity, the slower $\lim_{g \to 0^+} \Delta S/W$ converges to zero, and also the closer the efficiency is to the Carnot efficiency.

Using this lemma, we prove achievability of the Carnot efficiency which depends on Ω.

Lemma 7.10 (Quasi-static efficiencies as a function of $\bar{\kappa}$)**.** *For any $n \in \mathbb{Z}^+$ number of qubits, consider quasi-static heat engines (Def. 6.1) as a function of $\bar{\kappa}$ (defined in Lemma 7.6) which extract near perfect work (Def. 6.3). For any $\kappa \in (0,\infty)\backslash\{1\}$, define*

$$\gamma(\kappa) := \frac{\kappa B_\kappa}{\kappa - 1} \tag{7.4.48}$$

where B_κ is defined in Eq. (7.4.28), while $\gamma(1)$ and $\gamma(\infty)$ are defined by taking the limits $\kappa \to 1, \infty$ respectively.
If $\Omega \leq 1$ (see Eq. (7.4.47)):

1) There exists $\nu \in [0,1)$ *such that for any* $\bar{\kappa} \in (\nu, 1]$ *(and* $\lim_{g\to 0^+}(\varepsilon \ln \varepsilon)/g = 0$ *if* $\bar{\kappa} = 1$*), the maximum efficiency is*

$$\eta^{-1}(\bar{\kappa}) = 1 + \frac{\beta_h}{\beta_c - \beta_h}\frac{\gamma(1)}{\gamma(\bar{\kappa})} + \Theta(f(g)) + \Theta(g) + \Theta(\varepsilon), \tag{7.4.49}$$

where $\gamma(1) \geq \gamma(\bar{\kappa})$ *with equality iff* $\bar{\kappa} = 1$ *and* $\lim_{g\to 0+} f(g) = 0$.

2) The corresponding amount of work extracted is

$$W_{\text{ext}}(\bar{\kappa}) = \frac{ng}{\beta_h}\left[\gamma(\bar{\kappa}) + \Theta\left(f(g)\right)\right]. \tag{7.4.50}$$

If $\Omega > 1$*:*

1) There exists $\nu' \in [0,1)$ *such that for any* $\bar{\kappa} \in (\nu', 1]$ *(and* $\lim_{g\to 0^+}(\varepsilon \ln \varepsilon)/g = 0$ *if* $\bar{\kappa} = 1$*), the maximum efficiency is*

$$\eta^{-1}(\bar{\kappa}) = 1 + \frac{\beta_h}{\beta_c - \beta_h}\frac{\gamma(1)}{\gamma(\infty)} + \Theta(f(g)) + \Theta(g) + \Theta(\varepsilon), \tag{7.4.51}$$

where $\gamma(1) < \gamma(\infty)$.

2) The corresponding amount of work extracted is

$$W_{\text{ext}}(\bar{\kappa}) = g\frac{n}{\beta_h}\left[\gamma(\infty) + \Theta\left(f(g)\right)\right] \tag{7.4.52}$$

Proof. Firstly, let us begin by deriving the explicit form for $\gamma(1)$ and $\gamma(\infty)$:

$$\gamma(1) = \lim_{\alpha\to 1}\frac{\alpha}{\alpha - 1}B_\alpha = \lim_{\alpha\to 1} B_\alpha + \alpha B'_\alpha = B'_1 = \frac{E^2(\beta_c - \beta_h)}{(1 + e^{\beta_c E})^2}e^{\beta_c E}, \tag{7.4.53}$$

where we have made use of the L'Hôspital rule. For $\alpha \to \infty$, since

$$\lim_{\alpha\to\infty} B_\alpha = \lim_{\alpha\to\infty}\frac{E}{1 + e^{\beta_c E}}\frac{e^{\beta_h E} - e^{\beta_c E}e^{-\alpha(\beta_c - \beta_h)E}}{e^{\beta_h E} + e^{-\alpha(\beta_c - \beta_h)E}} = \frac{E}{1 + e^{\beta_c E}},$$

therefore we have

$$\gamma(\infty) = \lim_{\alpha\to 1}\left(1 + \frac{1}{\alpha - 1}\right)\cdot B_\alpha = \frac{E}{1 + e^{\beta_c E}}. \tag{7.4.54}$$

By Lemma 7.9, we know that the infimum of $\gamma(\alpha)$ for $\alpha \in [\bar{\kappa}, \infty)$ and $\bar{\kappa} \in (\nu, 1]$ is either at $\alpha = \bar{\kappa}$ or $\alpha \to \infty$. Therefore, if we take the ratio of Eqs. (7.4.53) and (7.4.54) to be

$$\frac{\gamma(1)}{\gamma(\infty)} = \frac{E(\beta_c - \beta_h)}{1 + e^{-\beta_c E}} = \Omega \leq 1, \tag{7.4.55}$$

then $\gamma(\infty) \geq \gamma(1) > \gamma(\bar{\kappa})$, therefore the infimum of $\gamma(\alpha)$ for $\alpha \in [\bar{\kappa}, \infty)$ and $\bar{\kappa} \in (\nu, 1]$ has to be obtained at $\alpha = \bar{\kappa}$. Taking this into account, we can use Lemmas 7.7 and 7.9 to calculate the amount of work extracted:

$$W_{\text{ext}} = \inf_{\alpha\geq 0} W_\alpha = g\cdot\left[\inf_{\alpha > \bar{\kappa}}\frac{n}{\beta_h}\gamma(\bar{\kappa}) + \Theta\left(f(g)\right)\right] = g\frac{n}{\beta_h}\left[\gamma(\bar{\kappa}) + \Theta\left(f(g)\right)\right], \tag{7.4.56}$$

where $\lim_{g\to 0+} f(g) = 0$. On the other hand, ΔC is the change of average energy in the cold bath system, (recall this is done by Taylor expansion around $g = 0$)

$$\Delta C = n\left(\langle E^2\rangle_{\beta_c} - \langle E\rangle^2_{\beta_c}\right)g + \Theta\left(g^2\right) = \frac{n\gamma(1)}{\beta_c - \beta_h}g + \Theta\left(g^2\right). \tag{7.4.57}$$

Using Eq. (6.5.14), we have $\Delta W = (1-\varepsilon)W_{\text{ext}}$. The (inverse) efficiency, according to the expression in Eq. (6.5.16) is then

$$\eta^{-1}(\bar{\kappa}) = 1 + \frac{\Delta C}{W_{\text{ext}}} - \varepsilon \tag{7.4.58}$$

$$= 1 + \frac{n\gamma(1)/(\beta_c - \beta_h)g + \Theta\left(g^2\right)}{n\gamma(\bar{\kappa})g/\beta_h + \Theta\left(gf(g)\right)} - \varepsilon \tag{7.4.59}$$

$$= 1 + \frac{\beta_h}{(\beta_c - \beta_h)}\frac{\gamma(1)}{\gamma(\bar{\kappa})} + \Theta(f(g)) + \Theta(g) + \Theta(\varepsilon), \tag{7.4.60}$$

where we have used $\lim_{g\to 0^+} f(g) = 0$ which is proven in Lemma 7.7.

Next, consider the efficiency when $\Omega > 1$ is satisfied. Using $\Omega > 1$ and Eq. (7.4.55), we have that $\gamma(\infty) < \gamma(1)$. Therefore, from Lemma 7.9, due to continuity of $\gamma(\bar{\kappa})$ in $\bar{\kappa}$, there exists a $\nu' \in [0,1)$ such that for any $\bar{\kappa} \in (\nu', 1]$,

$$\inf_{\alpha\geq\bar{\kappa}} \gamma(\alpha) = \gamma(\infty). \tag{7.4.61}$$

Since for near perfect work, Eq. (6.3.2) holds and therefore Lemma 7.7 can be used to calculate the amount of work extracted

$$W_{\text{ext}} = \inf_{\alpha\geq 0} W_\alpha = g\cdot\left[\inf_{\alpha>\bar{\kappa}} \frac{n}{\beta_h}\gamma(\bar{\kappa}) + f(g)\right] = g\frac{n}{\beta_h}\left[\gamma(\infty) + \frac{\beta_h}{n}f(g)\right], \tag{7.4.62}$$

where $\lim_{g\to 0+} f(g) = 0$. Therefore, the inverse efficiency is

$$\eta^{-1}(\bar{\kappa}) = 1 + \frac{\Delta C}{W_{\text{ext}}} - \varepsilon \tag{7.4.63}$$

$$= 1 + \frac{n\gamma(1)/(\beta_c - \beta_h)g + \Theta\left(g^2\right)}{n\gamma(\infty)g/\beta_h + \Theta\left(gf(g)\right)} - \varepsilon \tag{7.4.64}$$

$$= 1 + \frac{\beta_h}{(\beta_c - \beta_h)}\frac{\gamma(1)}{\gamma(\infty)} + \Theta(f(g)) + \Theta(g) + \Theta(\varepsilon), \tag{7.4.65}$$

where we have used $\lim_{g\to 0^+} f(g) = 0$ which is proven in Lemma 7.7. □

Finally, Lemma 7.10 can be used to make a statement regarding the maximum achievable efficiency $\eta^{\text{nano}}_{\text{max}}$. This is summarized in Lemma 7.11.

Lemma 7.11. *Consider a QHE where the cold bath consists of n identical qubits with energy gap E, and Ω as defined in Eq. (7.4.47). If near perfect work is extracted, then:*

1) If $\Omega \leq 1$*, the maximum efficiency* $\eta_{\max}^{\text{nano}}$ *(see Eq.* (6.5.3)*) is the Carnot efficiency:*

$$\eta_{\max}^{\text{nano}} = \left(1 + \frac{\beta_h}{\beta_c - \beta_h}\right)^{-1} = \eta_C. \tag{7.4.66}$$

Furthermore, this efficiency is achieved only *for quasi-static heat engines, i.e.* $\eta_{\max} = \eta_{\max}^{\text{stat,nano}}$ *(see Eq.* (6.5.7)*).*

2) If $\Omega > 1$ *and the heat engine is quasi-static, then the achievable efficiency is*

$$\eta_{\max}^{\text{stat,nano}} = \left(1 + \frac{\beta_h}{\beta_c - \beta_h}\Omega\right)^{-1} < \eta_C. \tag{7.4.67}$$

3) If $\Omega > 1$ *the maximum efficiency* $\eta_{\max}^{\text{nano}}$ *is strictly less than the Carnot efficiency.*

Proof. In Lemma 6.5, it is shown that the Carnot Efficiency always provides an upper bound on $\eta_{\max}^{\text{nano}}$ when considering near perfect work. In Lemma 7.10, we derived the optimal achievable efficiency for quasi-static heat engines as a function of $\bar{\kappa}$ when near perfect work is extracted. If $\Omega \leq 1$ is satisfied, according to Lemma 7.10, we can choose $\bar{\kappa} < 1$ but arbitrarily close to one, thus achieving an efficiency arbitrarily close to the Carnot efficiency. Thus since the upper bound is equal to the lower bound, we prove Item 1) of the Theorem.

Similarly, if $\Omega > 1$, we may prove Item 2) by noting that in Lemma 7.10, we have seen that the condition $\Omega > 1$ is equivalent to $\gamma(1) > \gamma(\infty)$. This implies already that the Carnot efficiency can never be achieved. By Lemma 7.10, there exists a regime $\bar{\kappa} \in (\nu', 1]$ where $\nu' < 1$, such that the achievable efficiency of the quasi-static heat engine (in the limit $g \to 0$) is given by

$$\eta_{\max}^{\text{stat,nano}} = \left(1 + \frac{\beta_h}{\beta_c - \beta_h}\frac{\gamma(1)}{\gamma(\infty)}\right)^{-1} = \left(1 + \frac{\beta_h}{\beta_c - \beta_h}\Omega\right)^{-1} < \eta_C. \tag{7.4.68}$$

Item 3) follows from Item 2), and the fact that we have established in Eq. (7.3.9) of Section 7.3.2 that the maximum achievable efficiency $\eta_{\max}^{\text{nano}}$can only be achieved by a quasi-static heat engine. □

NON-IDENTICAL QUBITS

By making use of Lemma 7.10, one can generalize Lemma 7.11 to consider the more general case stated in Assumption (A.5) at the beginning of Section 7.4.2, where the cold bath consists of n non-identical qubits. For convenience, we rewrite the general cold bath Hamiltonian here: for a set of variables $E_1, \cdots, E_n > 0$,

$$\hat{H}_{\text{Cold}} = \sum_{k=1}^{n} \mathbb{1}^{\otimes(k-1)} \otimes \hat{H}_{\text{c}}^k \otimes \mathbb{1}^{\otimes(n-k)}, \quad \text{where} \quad \hat{H}_{\text{c}}^k = E_k |E_k\rangle\langle E_k|, \tag{7.4.69}$$

With such a cold bath, we have the following theorem:

Theorem 7.1. *Consider a QHE with a cold bath consisting of n qubits with energy gaps* $\{E_i\}_{i=1}^n$*, and* Ω *as defined in Eq.* (7.4.47)*. If near perfect work is extracted, then*

1) If $\Omega \leq 1$, the maximum efficiency $\eta_{\max}^{\text{nano}}$ (see Eq. (6.5.3)) is the Carnot efficiency:

$$\eta_{\max}^{\text{nano}} = \left(1 + \frac{\beta_h}{\beta_c - \beta_h}\right)^{-1} = \eta_C. \tag{7.4.70}$$

Furthermore, this efficiency is achieved only *for quasi-static heat engines, i.e. $\eta_{\max} = \eta_{\max}^{\text{stat,nano}}$ (see Eq. (6.5.7)).*

2) If $\Omega > 1$ and the heat engine is quasi-static, then the achievable efficiency is

$$\eta_{\max}^{\text{stat,nano}} = \left(1 + \frac{\beta_h}{\beta_c - \beta_h}\Omega\right)^{-1} < \eta_C. \tag{7.4.71}$$

3) If $\Omega > 1$ the maximum efficiency $\eta_{\max}^{\text{nano}}$ is strictly less than the Carnot efficiency.

Proof. 1) is simple to prove: as long as there exists a qubit with energy E_i such that $\frac{E_i(\beta_c-\beta_h)}{1+e^{-\beta_h E_i}} \leq 1$, a straightforward way to achieve Carnot efficiency is to simply disregard the rest of the cold bath, and act only on such qubits. The result is a simple application of 1) in Lemma 7.11, by noting that the achievement of Carnot efficiency does not depend on the number of qubits involved (as long as there is 1 qubit that satisfies the condition). This strategy might be sub-optimal in terms of work extracted, but it is sufficient for our proof.

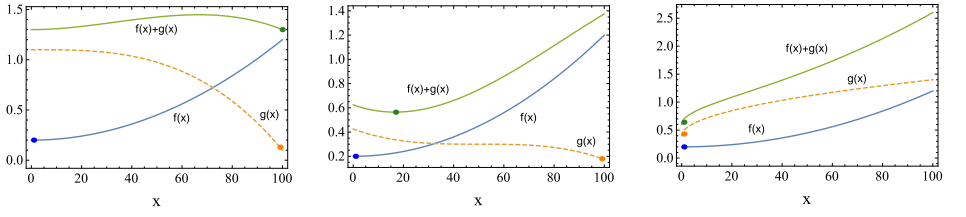

Figure 7.6: Illustration of the minima of two individual functions $f(x), g(x)$ and minima of $f(x) + g(x)$.

For 2) and 3), suppose that $\Omega > 1$. Since Ω is a monotonic function of E, we conclude that for all E_i where $1 \leq i \leq n$, $\Omega_i := \frac{E_i(\beta_c-\beta_h)}{1+e^{-\beta_h E_i}} > 1$. By Lemma 7.10, we see that this implies that the work extractable for all the individual qubits (which is an optimization problem over all $\alpha \geq 0$) is obtained at $\alpha \to \infty$. In general, considering the qubits collectively does not mean that the collective W_{ext} is additive. This is because the minima of two functions is not necessarily the minima of these individual functions added together, as illustrated in the leftmost and middle diagrams of Figure. 7.6. However, (as illustrated on rightmost diagram of Figure. 7.6), if all the functions have their minima at the same value, then the collective minima is also obtained at that value[3].

With this in mind, we show that no matter which subset of qubits $\mathscr{S}$ one picks, Carnot efficiency cannot be achieved. We begin by introducing the notation $\gamma_i(\alpha)$, where $\gamma_i(\alpha)$

[3]More rigorously, consider two functions $f(x)$ and $g(x)$ such that $\min_x f(x) = f(x^*)$ and $\min_x g(x) = g(x^*)$. On one hand, it holds that $\min_x [f(x) + g(x)] \geq \min_x f(x) + \min_x g(x) = f(x^*) + g(x^*)$. However, for any value of x^*, $f(x^*) + g(x^*) \geq \min_x f(x) + g(x)$. Therefore, $\min_x f(x) + g(x) = f(x^*) + g(x^*)$.

is defined in the same way with $\gamma(\alpha)$ in Eq. (7.4.48), but the index i indicates that E is substituted by E_i. Furthermore, recall that from Eq. (7.4.55), $\Omega_i > 1$ is equivalent to having $\gamma_i(1) > \gamma_i(\infty)$. Now, consider any subset of qubit indices $\mathscr{S}$, the amount of extractable work (as a function of g) is

$$W_{\text{ext}}^{\mathscr{S}} = \frac{g}{\beta_h}\left[\sum_{i\in\mathscr{S}} \gamma_i(\infty) + f(g)\right], \tag{7.4.72}$$

where $\lim_{g\to 0+} f(g) = 0$.

On the other hand, we have that ΔC depends on the individual reduced qubit states, since there are no interaction terms in $\hat{H}_{\text{Cold}}$. Therefore, similar to Eq. (7.4.57),

$$\Delta C^{\mathscr{S}} = \frac{g}{\beta_c - \beta_h}\sum_{i\in\mathscr{S}} \gamma_i(1) + \Theta\left(g^2\right). \tag{7.4.73}$$

Following the same proof in Eq. (7.4.63) of Lemma 7.10,

$$\eta^{-1}(\bar{\kappa}) = 1 + \frac{\Delta C}{W_{\text{ext}}} - \varepsilon = 1 + \frac{\beta_h}{\beta_c - \beta_h}\frac{\sum_{i\in\mathscr{S}}\gamma_i(1)}{\sum_{i\in\mathscr{S}}\gamma_i(\infty)} + \Theta(g) + \Theta(\varepsilon). \tag{7.4.74}$$

In order to maximize efficiency, one is left to pick a subset $\mathscr{S}$ such that the quantity $\frac{\sum_{i\in\mathscr{S}}\gamma_i(1)}{\sum_{i\in\mathscr{S}}\gamma_i(\infty)}$ is minimized. It is straightforward to see that this subset $\mathscr{S} = \{i|\Omega_i = \Omega\}$ should only contain indices such that Ω_i achieves the minimum value Ω. Therefore, the achievable efficiency in the limit $g \to 0$ is given by

$$\eta_{\max}^{\text{stat,nano}} = \left(1 + \frac{\beta_h}{\beta_c - \beta_h}\Omega\right)^{-1} < \eta_C. \tag{7.4.75}$$

Lastly, Item 3) follows with the exact same argument as in Lemma 7.11. □

7

RECOVERING CARNOT EFFICIENCY IN THE LIMIT OF MANY QUBITS

Suppose n is large. Then since we have a spectrum which looks like a quasi-continuum: the full range of the spectrum is very large, compared to the individual energy gaps. One expects that in such a case, baths are of much higher temperature (relatively small values of β_c, β_h), then the effects of quantization should give us the classical observations of being able to achieve Carnot always.

This can be seen, that for $E_{\min} = \min_{i\in\{1,\cdots,n\}} E_i$, if the quantities $\beta_c E_{\min}, \beta_h E_{\min} \ll 1$, then

$$\Omega = \frac{E_{\min}(\beta_c - \beta_h)}{1 + e^{-\beta_c E_{\min}}} \leq E_{\min}(\beta_c - \beta_h) \ll 1. \tag{7.4.76}$$

Whenever $\Omega \leq 1$, by Theorem 7.1 Carnot efficiency is achievable.

7.4.4. MULTIPLE QUASI-STATIC CYCLES OF A QHE

So far, it has been proven that a heat engine may achieve the Carnot efficiency when $\Omega \leq 1$. However, this can only be achieved when the heat engine is quasi-static, and in this limit, the amount of work extracted is infinitesimally small. However, we show in the subsequent lemma that when $\Omega \leq 1$, a QHE with a machine that runs over infinitely many cycles can

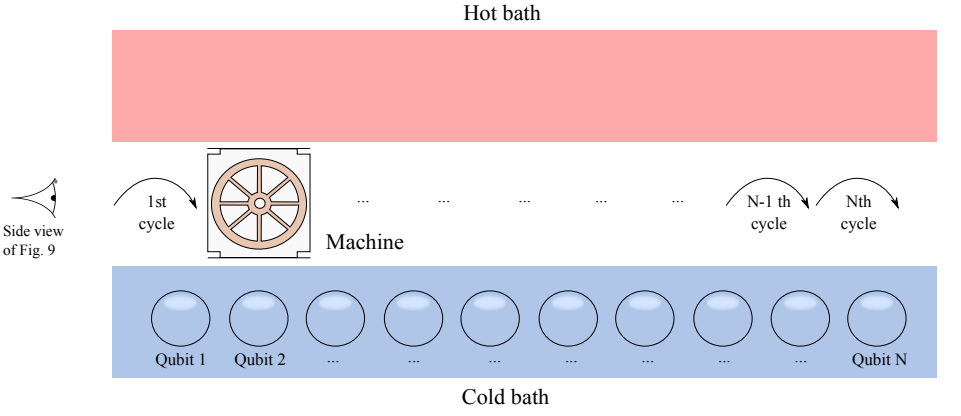

Figure 7.7: Depiction (top view) of a heat engine comprising of a hot bath, a cold bath consisting of n identical qubits, a machine and a battery. In each cycle, the machine interacts specifically with one qubit from the cold bath, together with the hot bat and battery. After the end of one cycle, the machine is returned to its original state, and acts on a different qubit in the cold bath.

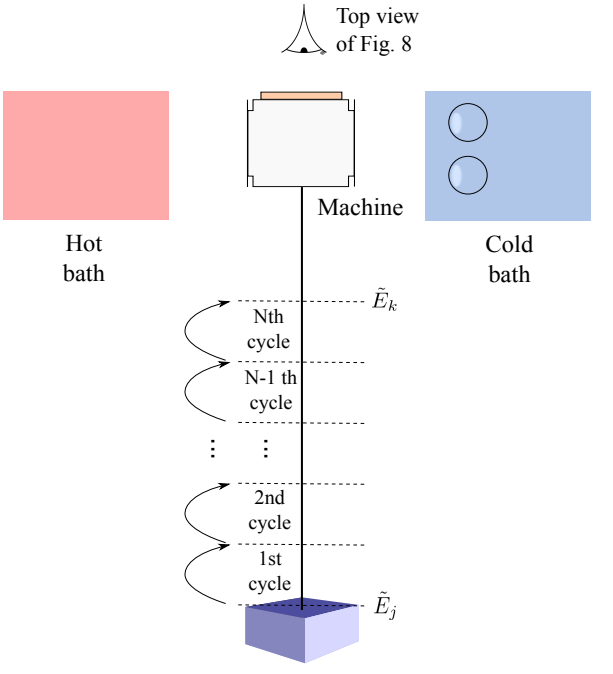

Figure 7.8: Side view of the heat engine. After each cycle of the machine, the battery, depicted here as a weight moves upward by a small amount. After N machine cycles, it has been lifted from its original position $|\tilde{E}_j\rangle$ to a final state that has most of its weight on $|\tilde{E}_k\rangle$.

also achieve the Carnot efficiency, while extracting a finite amount of work W with an arbitrarily small entropy increase in the battery.

For simplicity, we will work with the case in which the quasi-continuum battery has a part of its spectrum equal to that of at least N qubits, each with an energy gap W_{ext}. Let $\tilde{E}_j$ and $\tilde{E}_k$ be the smallest and largest energy eigenvalues within this battery subspace. We only use this subspace of the battery. The heat engine is operated between a hot bath, cold bath using a machine which undergoes N cycles. We let the initial state of the battery be

$$\rho_{\text{W}}^0 = |\tilde{E}_j\rangle\langle\tilde{E}_j|, \tag{7.4.77}$$

while we wish the final state of the battery to be of the form

$$\rho_{\text{W}}^1 = r|\tilde{E}_k\rangle\langle\tilde{E}_k| + (1-r)\,\rho_\psi, \tag{7.4.78}$$

ρ_ψ is a state orthogonal to $|\tilde{E}_k\rangle$, and $r \in (0,1)$ is to be specified in the subsequent lemma. We define the amount of work extracted from the machine for N cycles

$$W_{\text{cyc}} := \tilde{E}_k - \tilde{E}_j. \tag{7.4.79}$$

For simplicity, we will consider the case where the cold bath consists of n identical qubits with $\Omega \leq 1$, and during each cycle the machine interacts with one qubit from the cold bath. The operation of the heat engine is depicted in Fig. 7.7 and 7.8.

Corollary 7.1. *For any finite amount of work W we wish to extract, and any parameter $\delta > 0$ there exists an n-identical qubit cold bath with $\Omega \leq 1$, and an $N \in \mathbb{N}^+$ number of machine cycles with $n \geq N$ such that:*

1) *The amount of extractable work is $W_{\text{cyc}} \geq W - \delta$,*
2) *The amount of entropy in the battery is given by $S(\rho_{\text{W}}^0) = 0$, $S(\rho_{\text{W}}^1) \leq \delta$[4],*
3) *The probability of extracting the amount of work W_{cyc} is $r \geq 1 - \delta$, and*
4) *the maximum efficiency $\eta = \eta_C$ is given by Carnot efficiency.*

Proof. Since in the qubit subspace, the spectrum is that of at least N qubits, we can write the initial state in the form

$$\rho_{\text{W}}^0 = |E_j\rangle\langle E_j|^{\otimes N}, \tag{7.4.80}$$

with $\hat{H}_{\text{W}}|E_j\rangle^{\otimes N} = \tilde{E}_j|E_j\rangle^{\otimes N}$. One can now, however, apply the results of Lemma 7.10 in each of the N cycles. According to Lemma 7.10, each cycle will result in the battery qubit transition $|E_j\rangle\langle E_j| \to (1-\varepsilon)|E_k\rangle\langle E_k| + \varepsilon|E_j\rangle\langle E_j|$, where $\varepsilon(g)$ is a function of the quasi-static parameter g, and we may choose the characteristic parameter $\bar{\kappa} \in (0,1)$ for near perfect work extraction. The final state of the battery is thus

$$\rho_{\text{W}}^1 = \left[(1-\varepsilon)|E_k\rangle\langle E_k| + \varepsilon|E_j\rangle\langle E_j|\right]^{\otimes N}. \tag{7.4.81}$$

[4]Recall that this implies near perfect work is drawn.

Noting that $|\tilde{E}_k\rangle\langle\tilde{E}_k| = |E_k\rangle\langle E_k|^{\otimes N}$ by definition, Eq. (7.4.81) can be written as

$$\rho_{\mathrm{W}}^{1} = (1-\varepsilon)^{N}|\tilde{E}_k\rangle\langle\tilde{E}_k| + \left[1-(1-\varepsilon)^{N}\right]\rho_{\psi}. \tag{7.4.82}$$

with ρ_ψ orthogonal to $|\tilde{E}_k\rangle$. From Eq. (7.4.79) it follows,

$$W_{\mathrm{cyc}} = NW_{\mathrm{ext}} = \frac{Ng}{\beta_h}\left[\gamma(\bar{\kappa}) + \Theta\big(f(g)\big)\right], \tag{7.4.83}$$

where in the last line we have used Eq. (7.4.50). We now set

$$N = N(g) = \frac{\beta_h}{\gamma(\bar{\kappa})}\frac{W}{g} \tag{7.4.84}$$

for all $g > 0$ satisfying the constraint $N(g) \in \mathbb{N}^+$. For any positive constant $\frac{\beta_h W}{\gamma(\bar{\kappa})} > 0$, one can always consider the values of $\frac{\beta_h W}{\gamma(\bar{\kappa})} > g > 0$ so that $N(g)$ is large. This constraint imposes $g = \beta_h W/(\gamma(\bar{\kappa})N)$, where N has to be an integer. Therefore, g now belongs to a subset of the positive real line, rather than the positive real line itself as previously. However, since g monotonically decreases to zero as N increases to infinity, we can still take the limit $g \to 0^+$ as before, thus achieving

$$W_{\mathrm{cyc}} = W + \Theta\big(f(g)\big). \tag{7.4.85}$$

Since $\lim_{g\to 0^+} f(g) = 0$, we conclude Item 1).

The entropy of the final state of the battery can be calculated as

$$S(\rho_{\mathrm{W}}^{1}) = NS\left((1-\varepsilon)|E_k\rangle\langle E_k| + \varepsilon|E_j\rangle\langle E_j|\right) = \frac{\beta_h W}{\gamma(\bar{\kappa})}\frac{(1-\varepsilon)\ln(1-\varepsilon) + \varepsilon\ln\varepsilon}{g} = \Theta\left(\frac{\varepsilon\ln\varepsilon}{g}\right). \tag{7.4.86}$$

Furthermore, recall from the proof of Lemma 7.7 that $\lim_{g\to 0^+}\frac{\varepsilon\ln\varepsilon}{g} = 0$, for all $\bar{\kappa} \in (0,1)$. Thus, from Eq. (7.4.86) we conclude that 2) in Corollary 7.1 holds.

We will now prove part 3) of the Corollary. From Eq. (7.4.82) and part 3) of the Corollary, we can identify $r = (1-\varepsilon)^N$. We thus study the limit

$$\lim_{g\to 0^+}(1-\varepsilon)^{N} = \left(\lim_{g\to 0^+}(1-\varepsilon)^{1/g}\right)^{\beta_h W/\gamma(\bar{\kappa})} \tag{7.4.87}$$

$$= \left(\lim_{g\to 0^+}\left(\underbrace{(1-\varepsilon)^{1/\varepsilon}}_{\to \mathrm{e}}\right)^{\varepsilon/g}\right)^{\beta_h W/\gamma(\bar{\kappa})} \tag{7.4.88}$$

$$= 1, \tag{7.4.89}$$

where going to the last line, we have used that fact that since $\lim_{g\to 0^+}\frac{\varepsilon\ln\varepsilon}{g} = 0$, it also implies that $\varepsilon/g \to 0$ as $g \to 0^+$. This concludes Item 3).

Finally, Item 4) follows directly by noting that ΔC is additive over the amount of cycles, and so is W_{cyc} as shown in Eq. (7.4.83). Therefore, $\eta = 1 - \varepsilon + \frac{N\Delta C}{NW_{\text{ext}}} = \eta_C$, since by Lemma 7.11, in each individual cycle Carnot efficiency can be achieved. □

Therefore, by choosing $\delta > 0$ sufficiently small in Corollary 7.1, we can extract any finite amount of work with an arbitrarily small entropy contribution, and also with an efficiency arbitrarily close to the Carnot efficiency as long as $\Omega \leq 1$.

7.5. EXTENSIONS TO THE SETUP

Arguably, one may think that the inability to always achieve the Carnot efficiency η_C for QHEs is due to some subtlety of our setup (even though in Chapter 6 it has been shown that according to the macroscopic laws of thermodynamics, one can always achieve the Carnot efficiency with the setup). For such reasons, in the next few sections it is shown that even under more general conditions than those laid out in Section 6.2, one still cannot achieve the Carnot efficiency when $\Omega > 1$.

In Section 7.5.1, we show that allowing for correlations between the final state of the battery and cold bath (and/or the finite dimensional machine) does not allow us to achieve the Carnot efficiency. The main result is summarized in Theorem 7.2.

In Section 7.5.2, we show that allowing for the battery to be *any* state with trace distance ε from $|E_k\rangle\langle E_k|_{\text{W}}$ still does not allow us to achieve η_C when $\Omega > 1$. This shows that whenever we are unable to achieve the Carnot efficiency, it is not a artificial defect from an overly specified battery model. The main result is summarized in Theorem 7.3.

7.5.1. FINAL CORRELATIONS BETWEEN BATTERY, COLD BATH, AND MACHINE

In Section 7.3.1, we assumed that the final state of the heat engine after tracing out the hot bath was of tensor product form

$$\text{tr}_{\text{Hot}}(\rho^1_{\text{ColdHotMW}}) = \rho^1_{\text{Cold}} \otimes \rho^1_{\text{M}} \otimes \rho^1_{\text{W}}, \tag{7.5.1}$$

where $\rho^1_{\text{W}} = \varepsilon|E_j\rangle\langle E_j|_{\text{W}} + (1-\varepsilon)|E_k\rangle\langle E_k|_{\text{W}}$. We also demanded that the heat engine is cyclic i.e. that $\rho^1_{\text{M}} = \rho^0_{\text{M}}$. In this section, we show that if one allows for the final state of the battery, cold bath and machine to become correlated, while keeping the same restrictions on the reduced states $\rho^1_{\text{W}}, \rho^1_{\text{M}}$, one still cannot achieve the Carnot efficiency when $\Omega > 1$. That is to say, we allow the final state to be

$$\text{tr}_{\text{Hot}}(\rho^1_{\text{ColdHotMW}}) = \rho^1_{\text{ColdMW}} \tag{7.5.2}$$

with only two natural constraints, namely 1) that our heat engine actually extracts work, i.e. that $\rho^1_{\text{W}} = \varepsilon|E_j\rangle\langle E_j|_{\text{W}} + (1-\varepsilon)|E_k\rangle\langle E_k|_{\text{W}}$, as before, and also 2) that the heat engine is still cyclic, i.e. $\rho^1_{\text{M}} = \rho^0_{\text{M}}$. Throughout this section, (unless stated otherwise) we use ρ^1_{ColdMW} to denote any generic tripartite quantum state on the cold bath, machine and battery satisfying the above two constraints.

- We first define the generalized efficiency where one is allowed to consider correlated final states. We see that although this may potentially affect the amount of extractable

work W_{ext}, the amount of heat change in the bath remains the same, by making use of energy conservation and the fact that the global Hamiltonian $\hat{H}_{\text{ColdHotMW}}$ does not contain interaction terms between subsystems.

- We then make use of the generalized second law when $\alpha = 1$, in order to show that final correlations still prohibits the surpassing of Carnot efficiency. This is proven by noting that the von Neumann entropy is subadditive, and the result is summarized in Lemma 7.14.
- Finally, we turn to the case where $\Omega > 1$, where recall that without final correlations it is shown in Theorem 7.1 that Carnot efficiency cannot be achieved. We show that even when final correlations are allowed, Carnot efficiency remains unachievable.

DEFINING THE GENERALIZED EFFICIENCY

Let us recall that in Section 6.5.2, we established that if the following assumptions hold:

(i) the final reduced state of the battery ρ^1_{W} is fixed by Eq. (6.2.6),

(ii) the state of the machine is preserved, i.e. $\rho^0_{\text{M}} = \rho^1_{\text{M}}$,

(iii) the final state is of tensor product form, i.e. $\rho^1_{\text{ColdMW}} = \rho^1_{\text{Cold}} \otimes \rho^1_{\text{M}} \otimes \rho^1_{\text{W}}$,

then the efficiency for a particular transformation $\rho^0_{\text{ColdHotMW}} \to \rho^1_{\text{ColdHotMW}}$ simplifies to being only an explicit function of ρ^1_{Cold}. This simplified expression of the efficiency in Eq. (6.5.16) is then used to evaluate, for example, $\eta^{\text{mac}}(\rho^1_{\text{Cold}})$ in Eq. (6.5.4).

Since we now drop Assumption (iii) for the final state being uncorrelated, the efficiency and the work extracted W_{ext} will become dependent on the tripartite final state ρ^1_{ColdMW} instead. Therefore, let us first write a generalized expression for the maximum efficiency corresponding to a transition $\rho^0_{\text{ColdHotMW}} \to \rho^1_{\text{ColdHotMW}}$:

$$\eta^{\text{qm}}(\rho^1_{\text{ColdMW}}) := \sup_{W_{\text{ext}}} \eta(\rho^1_{\text{Cold}}, W_{\text{ext}}) \quad \text{s.t.} \quad \text{tr}_{\text{Hot}}[U \rho_{\text{ColdHotMW}} U^\dagger] = \rho^1_{\text{ColdMW}}, \tag{7.5.3}$$

$$[U, \hat{H}_{\text{ColdHotMW}}] = 0, \tag{7.5.4}$$

$$\rho^1_{\text{W}} = \varepsilon |E_j\rangle\langle E_j|_{\text{W}} + (1-\varepsilon)|E_k\rangle\langle E_k|_{\text{W}}, \tag{7.5.5}$$

$$\rho^1_{\text{M}} = \rho^0_{\text{M}}. \tag{7.5.6}$$

See Fig 6.1 for a definition of the other quantities appearing in Eq. (7.5.3). Recall that the definition of η is given by $\eta = W_{\text{ext}}/\Delta H$ as in Eq. (6.5.1). In Section 6.5.2 we showed that this can be simplified to

$$\eta = (1 - \varepsilon + \Delta C/W_{\text{ext}})^{-1}, \tag{7.5.7}$$

where $\Delta C = \Delta C(\rho^1_{\text{Cold}})$. This equation holds under Assumption (i) and (ii), together with the fact that the global Hamiltonian does not contain interaction terms between both baths, battery, and machine. Since the derivation of Eq. (7.5.7) does not require Assumption (iii), it still holds for a general tripartite final state ρ^1_{ColdMW}. However, dropping Assumption (iii) may potentially allow for larger values of W_{ext}, and therefore subsequently might affect

η^{qm}. For this reason we write $\eta^{\text{qm}} = \eta^{\text{qm}}(\rho^1_{\text{ColdMW}})$ to remind ourselves that it is a function of the entire final state ρ^1_{ColdMW}.

We have written $\eta = \eta(\rho^1_{\text{Cold}}, W_{\text{ext}})$ to explicitly show the W_{ext} dependency of η[5]. Throughout this section, we analyze Eq. (7.5.3) only in the case of *near perfect work* (recall Def. 6.3). For the purpose of our proofs, we need to define a new family of intermediate efficiencies. They provide the maximum possible efficiency, when considering only a particular instance $\alpha \geq 0$ of the generalized second laws. For any $\alpha \in [0, \infty)$, let us denote

$$\eta^{\text{qm}}_\alpha(\rho^1_{\text{ColdMW}}) = \sup_{W_{\text{ext}}} \ \eta(\rho^1_{\text{Cold}}, W_{\text{ext}}) \tag{7.5.8}$$

$$\text{s.t. } F_\alpha(\tau^0_{\text{Cold}} \otimes \rho^0_{\text{M}} \otimes \rho^0_{\text{W}}, \tau^h_{\text{ColdMW}}) \geq F_\alpha(\rho^1_{\text{ColdMW}}, \tau^h_{\text{ColdMW}}), \tag{7.5.9}$$

$$\text{tr}(\hat{H}_{\text{ColdHotMW}} \rho^0_{\text{ColdHotMW}}) = \text{tr}(\hat{H}_{\text{ColdHotMW}} \rho^1_{\text{ColdHotMW}}), \tag{7.5.10}$$

$$\rho^1_{\text{W}} = \varepsilon |E_j\rangle\langle E_j|_{\text{W}} + (1-\varepsilon)|E_k\rangle\langle E_k|_{\text{W}}, \tag{7.5.11}$$

$$\rho^1_{\text{M}} = \rho^0_{\text{M}}. \tag{7.5.12}$$

See Eq. (4.5.64) for definition of F_α. We denote $\eta^{\text{qm}}_\infty = \lim_{\alpha\to\infty} \eta^{\text{qm}}_\alpha$. The condition Eq. (7.5.10) is always satisfied when all the second laws are satisfied (i.e. when there exists a CTO that brings ρ^0_{ColdMW} to ρ^1_{ColdMW}). We add Eq. (7.5.10) as a constraint in this problem, since satisfying one of the α second laws does not necessarily guarantee the existence of such an energy preserving operation, but nevertheless we still need energy conservation in order to write the efficiency η in the form of Eq. (7.5.7).

CARNOT EFFICIENCY CANNOT BE SURPASSED

Proof Sketch

We show that Carnot efficiency η_C cannot be surpassed even when we allow arbitrary final correlations in the final state ρ^1_{ColdMW}. This is done in the following steps:

1. Using the definitions of generalized efficiency (allowing correlations) in Eq. (7.5.3) and generalized intermediate efficiencies in Eq. (7.5.8), we prove an inequality between $\eta^{\text{qm}}(\rho^1_{\text{ColdMW}})$ and $\eta^{\text{qm}}_\alpha(\rho^1_{\text{ColdMW}})$, for all $\alpha \geq 0$. This is done in Lemma 7.12. From this, we also conclude that $\eta^{\text{qm}}(\rho^1_{\text{ColdMW}}) \leq \eta^{\text{qm}}_1(\rho^1_{\text{ColdMW}})$.

2. On the other hand, we show that for any final state of the cold bath, machine and battery ρ^1_{ColdMW}, the generalized intermediate efficiency for $\alpha = 1$ only increases, if we consider the tensor product of the marginals ρ^1_{ColdMW}. In other words, $\eta^{\text{qm}}_1(\rho^1_{\text{ColdMW}}) \leq \eta^{\text{qm}}_1(\rho^1_{\text{Cold}} \otimes \rho^1_{\text{W}} \otimes \rho^1_{\text{M}})$. One can intuitively see why this is true: it comes from the fact that the von Neumann entropy is subadditive, therefore the final state $\rho^1_{\text{Cold}} \otimes \rho^1_{\text{W}} \otimes \rho^1_{\text{M}}$ contains more entropy than ρ^1_{ColdMW}. Therefore accord-

[5] Although not written explicitly in Eq. (7.5.3), we should remember that $U(t), \rho^0_{\text{M}}, \hat{H}_{\text{Hot}}$ and $\hat{H}_{\text{M}}$ are arbitrary, other than satisfying condition **(A.4)** in Section 6.2. As such, by maximizing η over W_{ext}, these quantities will accommodate their optimal values to maximize $\eta^{\text{qm}}(\rho^1_{\text{ColdMW}})$. This is an advantage, since it rules out cases such as when the Hamiltonian does not support a thermal state (e.g. when the corresponding thermal state's partition function diverges). In this section we consider any cold bath Hamiltonian $\hat{H}_{\text{Cold}}$ that satisfies **(A.6)** in Section 6.2 (i.e. finite dimensional). As such it will always have a well defined thermal state.

ing to the $\alpha = 1$ second law, one can potentially draw more work by going to the state $\rho^1_{\text{Cold}} \otimes \rho^1_{\text{W}} \otimes \rho^1_{\text{M}}$ instead of a correlated state ρ^1_{ColdMW}.

3. Since the final state yielding $\eta_1^{\text{qm}}(\rho^1_{\text{Cold}} \otimes \rho^1_{\text{W}} \otimes \rho^1_{\text{M}})$ is of tensor product form, Assumption (iii) holds, and the efficiency only depends on the final state of the cold bath ρ^1_{Cold}. This means that Eq. (7.5.8) for $\alpha = 1$ reduces to Eq. (6.5.4). Lastly, using Lemma 7.17 allows us to further show in Lemma 7.14 that even by allowing correlations in ρ^1_{ColdMW}, the efficiency $\eta^{\text{qm}}(\rho^1_{\text{ColdMW}})$ can never surpass η_C.

Firstly, let us fix the following notation: for an R-partite state $\rho_{\text{A}_1\text{A}_2\ldots\text{A}_R}$, define

$$\underline{\rho_{\text{A}_1\text{A}_2\ldots\text{A}_R}} := \bigotimes_{i=1}^{R} \rho_{\text{A}_i}. \tag{7.5.13}$$

Comparing $\rho_{\text{A}_1\text{A}_2\ldots\text{A}_R}$ and $\underline{\rho_{\text{A}_1\text{A}_2\ldots\text{A}_R}}$, one will see that each subsystem has the same reduced state, but the global state is different. Another useful thing is to note that if one is given a Hamiltonian which does not contain any interaction terms between each subsystem, i.e.

$$\hat{H}_{\text{A}_1\text{A}_2\ldots\text{A}_R} = \sum_{i=1}^{R} \mathbb{1}_{\text{A}_1} \otimes \cdots \hat{H}_{\text{A}_i} \cdots \mathbb{1}_{\text{A}_R}, \tag{7.5.14}$$

then we may conclude that

$$\text{tr}(\hat{H}_{\text{A}_1\text{A}_2\ldots\text{A}_R}\rho_{\text{A}_1\text{A}_2\ldots\text{A}_R}) = \sum_{i=1}^{R} \text{tr}(\hat{H}_{\text{A}_i}\rho_{\text{A}_i}) = \sum_{i=1}^{R} \text{tr}(\hat{H}_{\text{A}_i}\underline{\rho_{\text{A}_i}}) = \text{tr}(\hat{H}_{\text{A}_1\text{A}_2\ldots\text{A}_R}\underline{\rho_{\text{A}_1\text{A}_2\ldots\text{A}_R}}). \tag{7.5.15}$$

Lemma 7.12. *For all $\alpha \geq 0$ and all states $\rho^1_{\text{ColdHotMW}}$,*

$$\eta^{\text{qm}}(\rho^1_{\text{ColdMW}}) \leq \eta_\alpha^{\text{qm}}(\rho^1_{\text{ColdMW}}), \tag{7.5.16}$$

where η^{qm} and η_α^{qm} are defined in Eqs. (7.5.3) *and* (7.5.8) *respectively.*

Proof. To prove this lemma, one needs to show that the constraints for η^{qm} are a subset of those for η_α^{qm}. Note that the constraints on reduced states $\rho^1_{\text{W}}, \rho^1_{\text{M}}$ are identical for both quantities, so no comparison is needed. What remains is to see that given any unitary U that satisfies Eq. (7.5.3) and (7.5.4), then by the generalized second laws, the initial and final states will satisfy Eq. (7.5.9) for all $\alpha \geq 0$. Furthermore, since $[U, \hat{H}_{\text{ColdHotMW}}] = 0$, average energy is also preserved, and therefore Eq. (7.5.10) holds.

As a consequence of these observations, the set of allowed unitaries $U(t)$ in Eq. (7.5.3) is a subset of allowed transitions $\rho^0_{\text{ColdMW}} \to \rho^1_{\text{ColdMW}}$ in Eq. (7.5.8). □

Lemma 7.13. *For any final state ρ^1_{ColdMW}, consider the quantity $\eta_1^{\text{qm}}(\rho^1_{\text{ColdMW}})$ defined in*

Eq. (7.5.8)*. Consider the optimization problem*

$$a(\rho^1_{\text{ColdMW}}) := \sup_{W_{\text{ext}}} \ \eta(\rho^1_{\text{Cold}}, W_{\text{ext}}) \tag{7.5.17}$$

$$\text{s.t.} \ \ F_1(\tau^0_{\text{Cold}} \otimes \rho^0_{\text{M}} \otimes \rho^0_{\text{W}}, \tau^h_{\text{ColdMW}}) = F_1(\rho^1_{\text{ColdMW}}, \tau^h_{\text{ColdMW}}), \tag{7.5.18}$$

$$\text{tr}(\hat{H}_{\text{ColdHotMW}} \rho^0_{\text{ColdHotMW}}) = \text{tr}(\hat{H}_{\text{ColdHotMW}} \rho^1_{\text{ColdHotMW}}), \tag{7.5.19}$$

$$\rho^1_{\text{W}} = \varepsilon |E_j\rangle\langle E_j|_{\text{W}} + (1-\varepsilon)|E_k\rangle\langle E_k|_{\text{W}}, \tag{7.5.20}$$

$$\rho^1_{\text{M}} = \rho^0_{\text{M}}. \tag{7.5.21}$$

Then, $\eta_1^{\text{qm}}(\rho^1_{\text{ColdMW}}) = a(\rho^1_{\text{ColdMW}})$.

Proof. We begin by noting that the free energy F_1 can be written as

$$F_1(\rho, \tau^h) = \text{tr}(\hat{H}\rho) - \beta_h^{-1} S(\rho), \tag{7.5.22}$$

where $\langle \hat{H} \rangle_\rho := \text{tr}[\hat{H}\rho]$, and $S(\rho) = -\text{tr}(\rho \ln \rho)$ is the von Neumann entropy, while τ^h is the thermal state at inverse temperature β_h for the Hamiltonian $\hat{H}$. Also, let us recall that $W_{\text{ext}} = E^{\text{W}}_k - E^{\text{W}}_j > 0$ where E^{W}_j is a constant.

Next, we consider the free energies $F_1(\tau^0_{\text{Cold}} \otimes \rho^0_{\text{M}} \otimes \rho^0_{\text{W}}, \tau^h_{\text{ColdMW}})$ and $F_1(\rho^1_{\text{ColdMW}}, \tau^h_{\text{ColdMW}})$ respectively, and how they relate to W_{ext}. First of all, note that the quantity $F_1(\tau^0_{\text{Cold}} \otimes \rho^0_{\text{M}} \otimes \rho^0_{\text{W}}, \tau^h_{\text{ColdMW}})$ is simply a constant that does not depend on W_{ext}. This is because

$$\begin{aligned} F_1(\tau^0_{\text{Cold}} \otimes \rho^0_{\text{M}} \otimes \rho^0_{\text{W}}, \tau^h_{\text{ColdMW}}) &= F_1(\tau^0_{\text{Cold}}, \tau^h_{\text{Cold}}) + F_1(\tau^0_{\text{M}}, \tau^h_{\text{M}}) + F_1(\tau^0_{\text{W}}, \tau^h_{\text{W}}) \\ &= F_1(\tau^0_{\text{Cold}}, \tau^h_{\text{Cold}}) + F_1(\tau^0_{\text{M}}, \tau^h_{\text{M}}) + \text{tr}(\hat{H}_{\text{W}} \rho^0_{\text{W}}) - \beta_h^{-1} S(\rho^0_{\text{W}}) \\ &= F_1(\tau^0_{\text{Cold}}, \tau^h_{\text{Cold}}) + F_1(\tau^0_{\text{M}}, \tau^h_{\text{M}}) + E^{\text{W}}_j, \end{aligned}$$

where the first two terms do not depend on the battery Hamiltonian at all, while in the last equality we have made use of the fact that $\rho^0_{\text{W}} = |E_j\rangle\langle E_j|_{\text{W}}$. On the other hand,

$$\begin{aligned} F_1(\rho^1_{\text{ColdMW}}, \tau^h_{\text{ColdMW}}) &= \text{tr}(\hat{H}_{\text{ColdMW}} \rho^1_{\text{ColdMW}}) - \beta_h^{-1} S(\rho^1_{\text{ColdMW}}) \\ &= \text{tr}(\hat{H}_{\text{Cold}} \rho^1_{\text{Cold}}) + \text{tr}(\hat{H}_{\text{M}} \rho^1_{\text{M}}) + \text{tr}(\hat{H}_{\text{W}} \rho^1_{\text{W}}) - \beta_h^{-1} S(\rho^1_{\text{ColdMW}}) \\ &= \text{tr}(\hat{H}_{\text{Cold}} \rho^1_{\text{Cold}}) + \text{tr}(\hat{H}_{\text{M}} \rho^1_{\text{M}}) - \beta_h^{-1} S(\rho^1_{\text{ColdMW}}) + E^{\text{W}}_j + (1-\varepsilon) W_{\text{ext}}. \end{aligned}$$

Note that again, $\text{tr}(\hat{H}_{\text{Cold}} \rho^1_{\text{Cold}})$ and $\text{tr}(\hat{H}_{\text{M}} \rho^1_{\text{M}})$ do not depend on the battery Hamiltonian and therefore do not depend on E^{W}_k. Similarly, $S(\rho^1_{\text{ColdMW}})$ depends only on the eigenvalues of the state, and is independent of E^{W}_k. Since $1 - \varepsilon \in (0, 1]$, we may conclude the following: $F(\rho^1_{\text{ColdMW}}, \tau^h_{\text{ColdMW}})$ *is a continuous function that strictly increases w.r.t.* W_{ext}.

To prove this lemma, it suffices to show that the supremum over W_{ext} in Eq. (7.5.8) for $\alpha = 1$ is achieved when $F_1(\tau^0_{\text{Cold}} \otimes \rho^0_{\text{M}} \otimes \rho^0_{\text{W}}, \tau^h_{\text{ColdMW}}) = F_1(\rho^1_{\text{ColdMW}}, \tau^h_{\text{ColdMW}})$. We do this by contradiction: suppose $\hat{W}_{\text{ext}}$ achieves the supremum for η_1^{qm}, and for such value $\hat{W}_{\text{ext}}$,

$$F_1(\tau^0_{\text{Cold}} \otimes \rho^0_{\text{M}} \otimes \rho^0_{\text{W}}, \tau^h_{\text{ColdMW}}) > F_1(\rho^1_{\text{ColdMW}}, \tau^h_{\text{ColdMW}}).$$

Since $F(\rho^1_{\text{ColdMW}}, \tau^h_{\text{ColdMW}})$ is a continuous, strictly increasing function w.r.t. W_{ext}, there must exist an $W'_{\text{ext}} > \hat{W}_{\text{ext}}$ such that $F_1(\tau^0_{\text{Cold}} \otimes \rho^0_{\text{M}} \otimes \rho^0_{\text{W}}, \tau^h_{\text{ColdMW}}) \geq F_1(\rho^1_{\text{ColdMW}}, \tau^h_{\text{ColdMW}})$

also holds. Furthermore, since by Eq. (7.5.7) we know that the efficiency is strictly increasing w.r.t. W_{ext} as well, it follows that W'_{ext} achieves a higher value of efficiency compared to $\hat{W}_{\text{ext}}$ while satisfying the required constraints.

This is a contradiction, and therefore we conclude that the optimization for η_1^{qm} can be simplified to $a(\rho^1_{\text{ColdMW}})$, where the constraint on F_1 holds with equality. □

Lemma 7.14. *For any QHE with the final state $\rho^1_{\text{ColdHotMW}}$, then for perfect or near perfect work extraction (recall Defs. 6.2 and 6.3), we have*

$$\eta^{\text{qm}}\left(\rho^1_{\text{ColdMW}}\right) \overset{(1)}{\leq} \eta_1^{\text{qm}}\left(\rho^1_{\text{ColdMW}}\right) \overset{(2)}{\leq} \eta_1^{\text{qm}}\left(\underline{\rho^1_{\text{ColdMW}}}\right) \overset{(3)}{=} \eta^{\text{mac}}\left(\underline{\rho^1_{\text{Cold}}}\right) \overset{(4)}{\leq} 1-\frac{\beta_h}{\beta_c}, \tag{7.5.23}$$

with equality in (2) *iff* $\rho^1_{\text{ColdMW}} = \underline{\rho^1_{\text{ColdMW}}}$. *The quantities* η_1^{qm} *and* η^{mac} *are defined in Eq.* (7.5.8) *and Eq.* (6.5.4) *respectively.*

Proof. We begin by noting that inequality (1) is a direct consequence of Lemma 7.12, while inequality (4) holds because of Lemma 6.6. It remains to prove inequalities (2) and (3).
Proof of inequality (2): Using the definition in Eq. (7.5.8) together with Lemma 7.13, we compare the quantities

$$\begin{aligned}\eta_1^{\text{qm}}(\rho^1_{\text{ColdMW}}) = \sup_{W_{\text{ext}}}\ & \eta(\rho^1_{\text{Cold}}, W_{\text{ext}}) \\ \text{s.t. }\ & F_1(\tau^0_{\text{Cold}}\otimes\rho^0_{\text{M}}\otimes\rho^0_{\text{W}}, \tau^h_{\text{ColdMW}}) = F_1(\rho^1_{\text{ColdMW}}, \tau^h_{\text{ColdMW}}),\\ & \text{tr}(\hat{H}_t\rho^0_{\text{ColdHotMW}}) = \text{tr}(\hat{H}_t\rho^1_{\text{ColdHotMW}}),\\ & \rho^1_{\text{W}} = \varepsilon|E_j\rangle\langle E_j|_{\text{W}} + (1-\varepsilon)|E_k\rangle\langle E_k|_{\text{W}},\\ & \rho^1_{\text{M}} = \rho^0_{\text{M}},\end{aligned} \tag{7.5.24}$$

and

$$\begin{aligned}\eta_1^{\text{qm}}(\underline{\rho^1_{\text{ColdMW}}}) = \sup_{W_{\text{ext}}}\ & \eta(\underline{\rho^1_{\text{Cold}}}, W_{\text{ext}}) \\ \text{s.t. }\ & F_1(\tau^0_{\text{Cold}}\otimes\rho^0_{\text{M}}\otimes\rho^0_{\text{W}}, \tau^h_{\text{ColdMW}})F_1(\underline{\rho^1_{\text{ColdMW}}}, \tau^h_{\text{ColdMW}}),\\ & \text{tr}(\hat{H}_t\rho^0_{\text{ColdHotMW}}) = \text{tr}(\hat{H}_t\rho^1_{\text{ColdHotMW}}),\\ & \rho^1_{\text{W}} = \varepsilon|E_j\rangle\langle E_j|_{\text{W}} + (1-\varepsilon)|E_k\rangle\langle E_k|_{\text{W}},\\ & \rho^1_{\text{M}} = \rho^0_{\text{M}}.\end{aligned} \tag{7.5.25}$$

We first make the following observations:

- By definition of $\underline{\rho^1_{\text{ColdMW}}}$, we have that $\rho^1_{\text{Cold}} = \underline{\rho^1_{\text{Cold}}}$. Therefore, the term ΔC in Eq. (7.5.7) which is only a function of the reduced state on the cold bath is the same for both efficiencies in Eq. (7.5.24) and Eq. (7.5.25). To compare the efficiencies, we need only to compare the value of W_{ext} that satisfies the free energy constraint in both optimization problems.

- It is known that the von Neumann entropy is subadditive[6]

$$S(\rho_{AB}) \leq S\left(\underline{\rho_{AB}}\right), \tag{7.5.26}$$

with equality iff $\rho_{AB} = \underline{\rho_{AB}}$. Furthermore, since $\hat{H}_{\text{ColdMW}}$ does not contain interaction terms, as we have demonstrated earlier in Eq. (7.5.15),

$$\text{tr}(\hat{H}_{\text{ColdMW}}\rho^1_{\text{ColdMW}}) = \text{tr}(\hat{H}_{\text{ColdMW}}\underline{\rho^1_{\text{ColdMW}}}). \tag{7.5.27}$$

Thus, by Eq. (7.5.22) we conclude that

$$F_1(\underline{\rho^1_{\text{ColdMW}}}) \leq F_1(\rho^1_{\text{ColdMW}}), \tag{7.5.28}$$

with equality iff $\rho^1_{\text{ColdMW}} = \underline{\rho^1_{\text{ColdMW}}}$.

- For any final state ρ^1_{ColdMW} where $\rho^1_{\text{W}} = \varepsilon|E_j\rangle\langle E_j|_{\text{W}} + (1-\varepsilon)|E_k\rangle\langle E_k|_{\text{W}}$, we have seen in the proof of Lemma 7.13 that $F_1(\rho^1_{\text{ColdMW}}, \tau^h_{\text{ColdMW}})$ is a continuous function that strictly increases with W_{ext}.

With these three observations we can now prove inequality (2). Note that when $\rho^1_{\text{ColdMW}} = \underline{\rho^1_{\text{ColdMW}}}$, (2) holds trivially. Therefore, let us consider the case where $\rho^1_{\text{ColdMW}} \neq \underline{\rho^1_{\text{ColdMW}}}$. Suppose $\hat{W}_{\text{ext}}$ achieves the supremum in $\eta_1^{\text{qm}}(\rho^1_{\text{ColdMW}})$, and for such a value of $\hat{W}_{\text{ext}}$,

$$F_1(\tau^0_{\text{Cold}} \otimes \rho^0_{\text{M}} \otimes \rho^0_{\text{W}}, \tau^h_{\text{ColdMW}}) = F_1(\rho^1_{\text{ColdMW}}, \tau^h_{\text{ColdMW}}) \tag{7.5.29}$$

$$> F_1(\underline{\rho^1_{\text{ColdMW}}}, \tau^h_{\text{ColdMW}}). \tag{7.5.30}$$

Note that since $F_1(\underline{\rho^1_{\text{ColdMW}}}, \tau^h_{\text{ColdMW}})$ strictly increases with W_{ext}, therefore there exists $W'_{\text{ext}} > \hat{W}_{\text{ext}}$ such that W'_{ext} satisfies $F_1(\tau^0_{\text{Cold}} \otimes \rho^0_{\text{M}} \otimes \rho^0_{\text{W}}, \tau^h_{\text{ColdMW}}) = F_1(\underline{\rho^1_{\text{ColdMW}}}, \tau^h_{\text{ColdMW}})$. Therefore, W'_{ext} is a feasible solution for Eq. (7.5.25), i.e. it satisfies the constraints in the optimization problem. In conclusion, we have

$$\eta_1^{\text{qm}}(\rho^1_{\text{ColdMW}}) = \left[1 - \varepsilon + \frac{\Delta C}{\hat{W}_{\text{ext}}}\right]^{-1} \leq \left[1 - \varepsilon + \frac{\Delta C}{W'_{\text{ext}}}\right]^{-1} \leq \eta_1^{\text{qm}}(\underline{\rho^1_{\text{ColdMW}}}). \tag{7.5.31}$$

This proves inequality (2).

Proof of equality (3): Consider the quantity $\eta_1^{\text{qm}}(\underline{\rho^1_{\text{ColdMW}}})$. Since the state $\underline{\rho^1_{\text{ColdMW}}}$ takes on a product structure form between all the subsystems now, Assumption (iii) in the beginning of Section 7.5.1 holds again. By the third and fourth constraints in Eq. (7.5.24), we know that Assumptions (i) and (ii) also hold. Therefore, we know that under these assumptions the efficiency does not depend anymore on the global state $\underline{\rho^1_{\text{ColdMW}}}$, but only ρ^1_{Cold}. Again comparing the conditions of $\eta^{\text{mac}}(\underline{\rho^1_{\text{Cold}}})$ and $\eta_1^{\text{qm}}(\underline{\rho^1_{\text{ColdMW}}})$, we see that they are exactly the same quantity. □

Therefore, Lemma 7.14 tells us that correlations between the final states of the cold bath, machine and battery cannot allow us to surpass the Carnot efficiency.

[6]The reader may find a proof in page 395 of Ref. [176].

ACHIEVABILITY OF CARNOT EFFICIENCY STILL DEPENDS ON BATH HAMILTONIAN

Proof Sketch

Earlier, we proved in Lemma 7.14 that Carnot efficiency remains an upper bound to the efficiency of any arbitrary final state ρ^1_{ColdMW}. Here, we prove that when $\Omega > 1$ holds, one cannot achieve the Carnot efficiency even when allowing correlations between the final states of the battery and the cold bath. This is done in the following steps:

1. According to Lemma 7.14, Carnot efficiency can be attained only when all the inequalities in Eq. (7.5.23) are satisfied with equalities. We use this to prove in Lemma 7.15 that in order to achieve the Carnot efficiency, we may only consider the limit where correlations in the final state vanish. Not only so, the magnitude of these correlations also have to vanish quickly enough in order for Carnot efficiency to be achieved. In particular, we define a parameter k which quantifies the amount of correlations, and show that k has to vanish faster than the quasi-static parameter g, in order to achieve the Carnot efficiency η_C.

2. Next, in Lemma 7.16, we show that if the parameter k vanishes faster than the quasi-static parameter g, then whenever $\Omega > 1$, one can derive an upper bound for the intermediate efficiency $\eta^{\text{qm}}_{\infty}(\rho^1_{\text{ColdMW}})$ which considers the amount of work extractable by invoking only the generalized second law of $\alpha \to \infty$. Combining Lemma 7.15 and Lemma 7.16, we conclude in Corollary 7.2 that when $\Omega > 1$, $\eta^{\text{qm}} \leq \eta^{\text{qm}}_{\infty} < \eta_C$ is strictly upper bounded away from the Carnot efficiency.

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Before we begin, let us note that by definition, the initial state ρ^0_{ColdW} is block-diagonal. Furthermore, the state ρ^0_{ColdMW} is of the form $\rho^0_{\text{Cold}} \otimes \rho^0_{\text{M}} \otimes \rho^0_{\text{W}}$. Since w.l.o.g. we can assume that $\hat{H}_{\text{M}}$ is the trivial Hamiltonian, and ρ^0_{M} is always block-diagonal. Therefore the state ρ^0_{ColdMW} is always block-diagonal. Since catalytic thermal operations cannot create coherences [125], ρ^1_{ColdMW} has to be also block-diagonal in the energy eigenbasis of $\hat{H}_{\text{ColdMW}}$.

We observe that any ρ^1_{ColdMW} can always be written as

$$\rho^1_{\text{ColdMW}} = (1-k^*)\underline{\rho^1_{\text{ColdMW}}} + k^* \rho^{\text{corr}}_{\text{ColdMW}}, \tag{7.5.32}$$

where $k^* = \min\left\{k \in [0,1] \middle| \rho^1_{\text{ColdMW}} = (1-k)\underline{\rho^1_{\text{ColdMW}}} + kQ, Q \geq \mathbf{0}\right\}$. This means that ρ^1_{ColdMW} can be written as a convex combination of two states: one being $\underline{\rho^1_{\text{ColdMW}}}$, and the other $\rho^{\text{corr}}_{\text{ColdMW}}$ containing all other correlations. Note that such a k^* always exists, in particular, $k = 1$ is always a feasible solution.

We now define a particular parametrization of the final states,

$$\rho^1_{\text{ColdMW}}(k, \rho^{\text{no corr}}_{\text{ColdMW}}, \rho^{\text{corr}}_{\text{ColdMW}}) := (1-k)\rho^{\text{no corr}}_{\text{ColdMW}} + k\rho^{\text{corr}}_{\text{ColdMW}}, \quad k \in [0, k^*] \tag{7.5.33}$$

where the following holds:

$$\text{(i)}\ \ \rho^{\text{no corr}}_{\text{ColdMW}} = \underline{\rho^{1}_{\text{ColdMW}}}, \tag{7.5.34}$$

$$\text{(ii)}\ \ \rho^{\text{corr}}_{\text{ColdMW}} \neq \rho^{\text{no corr}}_{\text{ColdMW}}, \tag{7.5.35}$$

$$\text{(iii)}\ \ \rho^{1}_{\text{M}} = (1-k)\rho^{\text{no corr}}_{\text{M}} + k\rho^{\text{corr}}_{\text{M}} = \rho^{0}_{\text{M}}. \tag{7.5.36}$$

Since in our heat engine, the initial state has no coherences, it suffices to consider a block-diagonal final state ρ^{1}_{ColdMW}. This implies that $\rho^{\text{no corr}}_{\text{ColdMW}} = \underline{\rho^{1}_{\text{ColdMW}}}$ is also diagonal in the energy eigenbasis, and therefore the same holds for $\rho^{\text{corr}}_{\text{ColdMW}}$ due to Eq. (7.5.33). All correlations between the individual systems of cold bath, machine and battery are contained only in $\rho^{\text{corr}}_{\text{ColdMW}}$. Therefore, $\rho^{1}_{\text{ColdMW}}(\cdot,\cdot,\cdot)$ parametrizes every possible quantum state on $\mathscr{H}_{\text{ColdMW}}$ which is diagonal in the global energy eigenbasis and that returns the machine locally to its initial state after one cycle of the heat engine. In Eq. (7.5.36), ρ^{1}_{M} is the final state of the machine, since the heat engine is cyclic, recall that we require $\rho^{1}_{\text{M}} = \rho^{0}_{\text{M}}$.

Lemma 7.15. *Consider any family of states $\rho^{1}_{\text{ColdMW}}(k, \rho^{\text{no corr}}_{\text{ColdMW}}, \rho^{\text{corr}}_{\text{ColdMW}})$ parametrized by k, as detailed in Eqns. (7.5.33)-(7.5.36). If the quantum efficiency η_1^{qm} defined in Eq. (7.5.8) achieves the Carnot efficiency*

$$\eta_1^{\text{qm}}(\rho^{1}_{\text{ColdMW}}) = 1 - \frac{\beta_h}{\beta_c}, \tag{7.5.37}$$

then the following conditions are satisfied:

1) The state $\underline{\rho^{1}_{\text{ColdMW}}}$ is the final state of a quasi-static heat engine (see Def. 6.1)

$$\underline{\rho^{1}_{\text{ColdMW}}} = \tau(g) \otimes \rho^{0}_{\text{M}}(g) \otimes \rho^{1}_{\text{W}} \quad \textit{with } g \to 0^{+}. \tag{7.5.38}$$

2) The correlations must vanish sufficiently quickly. That is to say, the parameter k in Eq. (7.5.33) vanishes more quickly compared to g, i.e.

$$\lim_{g\to 0^{+}} \frac{k}{g} = 0. \tag{7.5.39}$$

Proof. Firstly, suppose that Carnot efficiency is achieved, i.e. $\eta^{\text{qm}}(\rho^{1}_{\text{ColdMW}}) = 1 - \frac{\beta_h}{\beta_c}$. Then according to Lemma 7.14, all inequalities in Eq. (7.5.23) should be satisfied with equality, in particular inequality (4). We have established in Lemma 6.6 that this equality is only achieved in the quasi-static limit, i.e. $\rho^{1}_{\text{Cold}} = \tau_{\text{Cold}}(g)$ where $g \to 0^{+}$. This implies Condition 1) in the statement of the lemma.

The proof for Condition 2) consists of calculating W_{ext} for $\alpha = 1$ in Eq. (7.5.8) to leading order in g and k. This W_{ext} quantity is later used to evaluate η_1^{qm}. We show that we can write the expression for η_1^{qm} into two terms: one term describes the efficiency when there are no final correlations, and the other term is a strictly negative contribution which must vanish in order to achieve Carnot efficiency. This latter constraint gives us Eq. (7.5.39).

Let us denote W'_{ext} as the value of energy gap $W_{\text{ext}} = E^{\text{W}}_{k} - E^{\text{W}}_{j}$ that solves

$$F_1(\tau^{0}_{\text{Cold}} \otimes \rho^{0}_{\text{M}}(g) \otimes \rho^{0}_{\text{W}}, \tau^{h}_{\text{ColdMW}}) = F_1(\rho^{1}_{\text{ColdMW}}(k, \rho^{\text{no corr}}_{\text{ColdMW}}, \rho^{\text{corr}}_{\text{ColdMW}}), \tau^{h}_{\text{ColdMW}})^{7}, \tag{7.5.40}$$

while $\hat{W}_{\text{ext}}$ as the value that solves the case where $k = 0$, i.e.

$$F_1(\tau^0_{\text{Cold}} \otimes \rho^0_{\text{M}}(g) \otimes \rho^0_{\text{W}}, \tau^h_{\text{ColdMW}}) = F_1(\rho^{\text{no corr}}_{\text{ColdMW}}, \tau^h_{\text{ColdMW}}). \tag{7.5.41}$$

Since $\rho^{\text{no corr}}_{\text{ColdMW}} = \underline{\rho^1_{\text{ColdMW}}} = \rho^1_{\text{Cold}} \otimes \rho^0_{\text{M}}(g) \otimes \rho^1_{\text{W}}$ contains no correlations, $\hat{W}_{\text{ext}}$ was given by Eq. (6.6.47). According to Lemma 7.13, we know that W'_{ext} and $\hat{W}_{\text{ext}}$ are the values of W_{ext} which solve $\sup_{W_{\text{ext}}} \eta_1^{\text{qm}}(\rho^1_{\text{ColdMW}}, W_{\text{ext}})$ and $\sup_{W_{\text{ext}}} \eta_1^{\text{qm}}(\underline{\rho^1_{\text{ColdMW}}}, W_{\text{ext}})$ respectively. Solving Eq. (7.5.41) for W'_{ext} with the aid of Eq. (7.5.22), we find

$$W'_{\text{ext}} = \hat{W}_{\text{ext}} - \chi, \tag{7.5.42}$$

where W_{ext} is the solution to Eq. (7.5.41) when $k = 0$, given by Eq. (6.6.47), while

$$\chi := \frac{1}{\beta_h} \frac{1}{1-\varepsilon} \left[S(\rho^{\text{no corr}}_{\text{ColdMW}}) - S\left(\rho^1_{\text{ColdMW}}(k, \rho^{\text{no corr}}_{\text{ColdMW}}, \rho^{\text{corr}}_{\text{ColdMW}})\right) \right]. \tag{7.5.43}$$

Let us first note some properties of χ, which we will later use:

- Since $S(\cdot)$ is subadditive, due to the parametrization of $\rho^1_{\text{ColdMW}}(\cdot,\cdot,\cdot)$ in Eq. (7.5.33), we have

  $$\chi \geq 0, \tag{7.5.44}$$

  with equality iff $\underline{\rho^1_{\text{ColdMW}}} = \rho^1_{\text{ColdMW}}$ (i.e. $k = 0$). Therefore, this implies $\frac{\hat{W}_{\text{ext}}}{W'_{\text{ext}}} \geq 1$.

- It holds that

  $$\frac{d}{dk}\chi(k, \rho^{\text{no corr}}_{\text{ColdMW}}, \rho^{\text{corr}}_{\text{ColdMW}})\Big|_{k=k_0} = 0 \tag{7.5.45}$$

  if and only if

  $$\rho^1_{\text{ColdMW}}(k_0, \rho^{\text{no corr}}_{\text{ColdMW}}, \rho^{\text{corr}}_{\text{ColdMW}}) = \mathbb{1}_{\text{ColdMW}}/N. \tag{7.5.46}$$

  Eqs. (7.5.45) and (7.5.46) are direct consequences of the observations:
  1) Entropy is strictly concave, i.e. $S\left(\rho^1_{\text{ColdMW}}(k, \rho^{\text{no corr}}_{\text{ColdMW}}, \rho^{\text{corr}}_{\text{ColdMW}})\right)$ is strictly concave in $k \in [0,1]$. Therefore, by Eq. (7.5.46) χ is strictly convex in $k \in [0,1]$. When the first derivative $\frac{d\chi}{dk} = 0$, this must be the global minimum [177].
  2) However, we know that the entropy is uniquely maximized (and therefore χ is uniquely minimized) for the maximally mixed state.

Returning to evaluate the efficiency, we use Eq. (7.5.7) to calculate

$$\begin{aligned}
[\eta_1^{\text{qm}}(\rho^1_{\text{ColdMW}})]^{-1} &= 1 - \varepsilon + \frac{\Delta C(\rho^1_{\text{Cold}})}{W'_{\text{ext}}} \\
&= 1 - \varepsilon + \frac{\Delta C(\rho^1_{\text{Cold}})}{\hat{W}_{\text{ext}}} \frac{\hat{W}_{\text{ext}}}{W'_{\text{ext}}} \\
&\geq 1 - \varepsilon + \frac{\Delta C(\rho^1_{\text{Cold}})}{\hat{W}_{\text{ext}}}.
\end{aligned} \tag{7.5.47}$$

The last inequality holds because we know the terms $\Delta C(\rho^1_{\text{Cold}}), \hat{W}_{\text{ext}}$ and W'_{ext} are all non-negative, while we have established that $\frac{\hat{W}_{\text{ext}}}{W'_{\text{ext}}} \geq 1$.

With Condition 1), we now know that

$$1 - \varepsilon + \frac{\Delta C(\rho^1_{\text{Cold}})}{W_{\text{ext}}} = 1 - \frac{\beta_h}{\beta_c},$$

in the quasi-static limit, and therefore a necessary condition to achieve the Carnot efficiency is that $\lim_{g\to 0} \frac{\hat{W}_{\text{ext}}}{W'_{\text{ext}}} = 1$ also in the quasi-static limit. Using the relation $W'_{\text{ext}} = \hat{W}_{\text{ext}} + \chi$, we have the requirement that

$$\lim_{g\to 0^+} \frac{\chi(k, \rho^{\text{no corr}}_{\text{ColdMW}}(g), \rho^{\text{corr}}_{\text{ColdMW}})}{\hat{W}_{\text{ext}}(\rho^{\text{no corr}}_{\text{ColdMW}}(g))} = 0.$$

First, let us observe that $\hat{W}_{\text{ext}}(\rho^{\text{no corr}}_{\text{ColdMW}}(g)) = W_{\text{ext}}(\beta_c - g)$ given by Eq. (6.6.36). The leading order term of $W_{\text{ext}}(\beta_c - g) = \Theta(g)$ as $g \to 0^+$. Therefore, in order to satisfy the above requirement, we must firstly have $\lim_{g\to 0} \chi = 0$. From Eqs. (7.5.33), (7.5.43), this implies that we need $k \to 0$ for all $\rho^{\text{no corr}}_{\text{ColdMW}}$.

Since the numerator and denominator of Eq. (7.5.48) both go to zero, by L'Hospital rule, to evaluate the limit we need to take the derivative of both terms w.r.t. g. Therefore, we expand χ to first order in k and g. From Eq. (7.5.43) it follows

$$\begin{aligned}\chi(k, \rho^{\text{no corr}}_{\text{ColdMW}}(g), \rho^{\text{corr}}_{\text{ColdMW}}) =& \frac{d}{dk}\chi(k, \rho^{\text{no corr}}_{\text{ColdMW}}(0), \rho^{\text{corr}}_{\text{ColdMW}})\Big|_{k=0} \cdot k \\ &+ \frac{d}{dg}\chi(0, \rho^{\text{no corr}}_{\text{ColdMW}}(g), \rho^{\text{corr}}_{\text{ColdMW}})\Big|_{g=0} \cdot g + o(gk) + o(k^2) + o(g^2) \\ =& \frac{d}{dk}\chi(k, \rho^{\text{no corr}}_{\text{ColdMW}}(0), \rho^{\text{corr}}_{\text{ColdMW}})\Big|_{k=0} k + o(gk) + o(k^2) + o(g^2).\end{aligned}$$

The term $\frac{d}{dg}\chi(0, \rho^{\text{no corr}}_{\text{ColdMW}}(g), \rho^{\text{corr}}_{\text{ColdMW}})\Big|_{g=0} = 0$ since when $k = 0$, χ will be constant for all g.

Next, we note that since Eqs. (7.5.44) holds, it must be that $\frac{d}{dk}\chi(k, \rho^{\text{no corr}}_{\text{ColdMW}}(0), \rho^{\text{corr}}_{\text{ColdMW}})\Big|_{k=0} \geq 0$. Furthermore, from Eq. (7.5.45), we have that

$$\frac{d}{dk}\chi(k, \rho^{\text{no corr}}_{\text{ColdMW}}(0), \rho^{\text{corr}}_{\text{ColdMW}})\Big|_{k=0} \neq 0, \tag{7.5.48}$$

for all $\rho^{\text{corr}}_{\text{ColdMW}}$ since by definition $\rho^1_{\text{ColdMW}}(0, \rho^{\text{no corr}}_{\text{ColdMW}}(0), \rho^{\text{corr}}_{\text{ColdMW}}) \neq \mathbb{1}_{\text{ColdMW}}/N$. We can infer that ρ^1_{ColdMW} is not maximally mixed from a few observations, for example: this is true because we have required that the reduced state on the battery is not maximally mixed since we consider near perfect work extraction.

Thus, taking into account $W_{\text{ext}}(\beta_c - g) = \Theta(g)$, Eq. (7.5.48) implies Eq. (7.5.39). □

By now, we have established a constraint on how quickly correlations have to vanish w.r.t. g, for the possibility of achieving Carnot efficiency. In the next Lemma 7.16, we show that the constraints given by Eq. (7.5.39) can be used to derive an upper bound for $\eta^{\text{qm}}_{\infty}$.

Lemma 7.16. *If Conditions 1) and 2) of Lemma 7.15 are satisfied, then the quantity* $\eta_\infty^{\mathrm{qm}}$ *can be upper bounded by*

$$\eta_\infty^{\mathrm{qm}}(\rho^1_{\mathrm{ColdMW}}(k,\rho^{\text{no corr}}_{\mathrm{ColdMW}}(g),\rho^{\mathrm{corr}}_{\mathrm{ColdMW}})) \leq \left[1+\frac{\beta_h}{\beta_c-\beta_h}\frac{\gamma(1)}{\gamma(\infty)}\right]^{-1}+\Theta(f(g))+\Theta(k/g)+\Theta(g)+\Theta(\varepsilon), \tag{7.5.49}$$

with $\lim_{g\to 0^+} f(g)=0$.

Proof. The main idea of our proof is as follows: we show that if Eqns. (7.5.38) and (7.5.39) hold, then we can upper bound W_{ext} while considering only the F_∞ condition. This bound only differs by a small amount from the value yielded when no correlations are present. Substituting this into the expression for $\eta_\infty^{\mathrm{qm}}$, we obtain Eq. (7.5.49).

Let us begin by analyzing the difference in eigenvalues of the states ρ^1_{ColdMW} and $\underline{\rho^1_{\mathrm{ColdMW}}}$. Recall that

$$\rho^1_{\mathrm{ColdMW}}(k,\rho^{\text{no corr}}_{\mathrm{ColdMW}},\rho^{\mathrm{corr}}_{\mathrm{ColdMW}})=(1-k)\rho^{\text{no corr}}_{\mathrm{ColdMW}}+k\rho^{\mathrm{corr}}_{\mathrm{ColdMW}} \tag{7.5.50}$$

where $\rho^{\text{no corr}}_{\mathrm{ColdMW}},\rho^{\mathrm{corr}}_{\mathrm{ColdMW}}$ are both block-diagonal. Since ρ^1_{ColdMW} is a mixture of two block-diagonal states, it is also block-diagonal. Let us denote its eigenvalues as $[\rho^1_{\mathrm{ColdMW}}]_i$.

As for $\underline{\rho^1_{\mathrm{ColdMW}}}$, Eqn. (7.5.38) gives the explicit form of the state,

$$\underline{\rho^1_{\mathrm{ColdMW}}}=\rho^1_{\mathrm{Cold}}\otimes\rho^1_{\mathrm{M}}\otimes\rho^1_{\mathrm{W}}=\tau(g)\otimes\rho^0_{\mathrm{M}}(g)\otimes\rho^1_{\mathrm{W}}. \tag{7.5.51}$$

Let us denote its eigenvalues as $[\underline{\rho^1_{\mathrm{ColdMW}}}]_i$.

We first observe two properties involving trace distance $d(\cdot,\cdot)$:

(P.i) Consider two states σ_1,σ_2 diagonal in the same eigenbasis. Then if $\rho=(1-k)\sigma_1+k\sigma_2$ for some $k\in[0,1]$, then one can conclude that the distance

$$d(\rho,\sigma_1)\leq k. \tag{7.5.52}$$

(P.ii) For any two states ρ,σ diagonal in the same basis, with eigenvalues p_i,q_i, if their trace distance

$$d(\rho,\sigma)\leq\varepsilon, \tag{7.5.53}$$

then this implies that their eigenvalues cannot differ by more than ε, i.e. $\forall i,|p_i-q_i|\leq\varepsilon$. By using this fact, we may first calculate the trace distance between ρ^1_{ColdMW} and $\underline{\rho^1_{\mathrm{ColdMW}}}$, then bound the difference of their eigenvalues.

We find that

$$d(\rho^1_{\mathrm{ColdMW}},\underline{\rho^1_{\mathrm{ColdMW}}})\leq d(\rho^1_{\mathrm{ColdMW}},\rho^{\text{no corr}}_{\mathrm{ColdMW}})+d(\rho^{\text{no corr}}_{\mathrm{ColdMW}},\underline{\rho^1_{\mathrm{ColdMW}}}) \tag{7.5.54}$$

$$\leq k+d(\rho^{\text{no corr}}_{\mathrm{Cold}},\rho^1_{\mathrm{Cold}})+d(\rho^{\text{no corr}}_{\mathrm{M}},\rho^1_{\mathrm{M}})+d(\rho^{\text{no corr}}_{\mathrm{W}},\rho^1_{\mathrm{W}}) \tag{7.5.55}$$

$$\leq 4k. \tag{7.5.56}$$

The first inequality is a triangle inequality that holds for all states. The second inequality holds because of (P.i), and because trace distance is subadditive under tensor product (note that both $\rho^{\text{no corr}}_{\text{ColdMW}}$ and $\underline{\rho^1_{\text{ColdMW}}}$ are tensor product states). The third inequality holds because we know $d(\rho^1_{\text{ColdMW}}, \rho^{\text{no corr}}_{\text{ColdMW}}) \leq k$ and that trace distance decreases under partial trace. By (P.ii), Eq. (7.5.56) tells us that $\forall i$,

$$[\rho^1_{\text{ColdMW}}]_i = [\underline{\rho^1_{\text{ColdMW}}}]_i + o(k). \tag{7.5.57}$$

With Eq.(7.5.57), we may relate the F_∞ quantities for the states ρ^1_{ColdMW} and $\underline{\rho^1_{\text{ColdMW}}}$. From the definition of F_∞, we have

$$\begin{aligned} F_\infty\big(\rho^1_{\text{ColdMW}}(k, \rho^{\text{no corr}}_{\text{ColdMW}}(g), \rho^{\text{corr}}_{\text{ColdMW}}), \tau^h_{\text{ColdMW}}\big) & \qquad (7.5.58)\\ = \ln \max_i \left\{ \frac{[\rho^1_{\text{ColdMW}}]_i}{\tau_i} \right\}, & \qquad (7.5.59)\\ = \ln \max_i \left\{ \frac{[\underline{\rho^1_{\text{ColdMW}}}]_i}{\tau_i} \right\} + o(k), & \qquad (7.5.60)\\ = F_\infty\left(\tau(g) \otimes \rho^0_{\text{M}}(g) \otimes \rho^1_{\text{W}}, \tau^h_{\text{ColdMW}}\right) + o(k), & \qquad (7.5.61) \end{aligned}$$

where we used Eq. (7.5.51) in the last line.

The next step is to evaluate the restriction on W_{ext} that satisfies

$$\begin{aligned} F_\infty(\tau^0_{\text{Cold}} \otimes \rho^0_{\text{M}} \otimes \rho^0_{\text{W}}, \tau^h_{\text{ColdMW}}) &\geq F_\infty\left(\rho^1_{\text{ColdMW}}(k, \rho^{\text{no corr}}_{\text{ColdMW}}(g), \rho^{\text{corr}}_{\text{ColdMW}}), \tau^h_{\text{ColdMW}}\right) & (7.5.62)\\ &= F_\infty\left(\tau(g) \otimes \rho^0_{\text{M}}(g) \otimes \rho^1_{\text{W}}, \tau^h_{\text{ColdMW}}\right) + o(k), & (7.5.63) \end{aligned}$$

for W_{ext} up to order $o(k)$. Taking into account the additivity of F_∞ under tensor product, we can rearrange Eq. (7.5.63) to provide an upper bound on W_{ext},

$$W_{\text{ext}} \leq \frac{ng}{\beta_h}\left[\gamma(\infty) + \Theta(f(g)) + o(k/g)\right], \tag{7.5.64}$$

where $\lim_{g\to 0^+} f(g) = 0$, $\gamma(\infty)$ is given by Eq. (7.4.54).

Lastly, we want to evaluate the intermediate efficiency η^{qm}_∞ as defined in Eq. (7.5.8). To do so, we use the expressions W_{ext} from Eq. (7.5.64) and ΔC from Eq. (7.4.57), and substitute them into the expression for efficiency in Eqs. (7.5.7), yielding

$$\begin{aligned} \eta^{\text{qm}}_\infty(\rho^1_{\text{ColdMW}}) &= \sup_{W_{\text{ext}}>0}\left(1 - \varepsilon + \frac{\Delta C}{W_{\text{ext}}}\right)^{-1} & (7.5.65)\\ &\leq \left[1 + \frac{\beta_h}{(\beta_c - \beta_h)}\frac{\gamma(1)}{\gamma(\infty)}\right]^{-1} + \Theta(f(g)) + o(k/g) + \Theta(g) + \Theta(\varepsilon), & (7.5.66) \end{aligned}$$

which proves the lemma. □

Finally, combining the above lemmas allow us to conclude that allowing further correlations in the final state cannot allow us to achieve Carnot efficiency when $\Omega > 1$.

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Theorem 7.2. *Suppose that $\Omega > 1$. Parametrizing the final state of the heat engine by Eq. (7.5.33)-(7.5.36) in order to consider correlations in the final state, the quantum efficiency η^{qm} defined in Eq. (7.5.3) is strictly upper bounded by the Carnot efficiency,*

$$\sup_{k\in[0,1],\ \rho^{\text{no corr}}_{\text{ColdMW}}} \eta^{\text{qm}}\left(\rho^{1}_{\text{ColdMW}}(k, \rho^{\text{no corr}}_{\text{ColdMW}}, \rho^{\text{corr}}_{\text{ColdMW}})\right) < 1 - \frac{\beta_h}{\beta_c}. \tag{7.5.67}$$

Proof. From Lemma 7.12, we have that both $\eta^{\text{qm}} \leq \eta^{\text{qm}}_1$ and $\eta^{\text{qm}} \leq \eta^{\text{qm}}_\infty$ hold. Thus a necessary condition to achieve the Carnot efficiency η_C for a particular ρ^{1}_{ColdMW}, is that both η^{qm}_1 and η^{qm}_∞ are equal to or greater than the Carnot efficiency.

Lemma 7.15 first proves that in order for $\eta_C \leq \eta^{\text{qm}}_1$, Eqs. (7.5.38) and (7.5.39) are necessary conditions for η^{qm}_1 to achieve Carnot efficiency. However, when Eqs. (7.5.38), (7.5.39) are satisfied, then Lemma 7.16 provides an upper bound on the efficiency η^{qm}_∞ in Eq. (7.5.49).

Now, suppose $\Omega > 1$. Since it is shown in Eq. (7.4.55) that $\gamma(1)/\gamma(\infty) = \Omega$, plugging this into the leading term appearing in Eq. (7.5.49)

$$\left[1 + \frac{\beta_h}{(\beta_c - \beta_h)} \frac{\gamma(1)}{\gamma(\infty)}\right]^{-1}, \tag{7.5.68}$$

we have that the quantity $\eta^{\text{qm}}_\infty < \eta_C$ is strictly less than the Carnot efficiency. Therefore, $\eta^{\text{qm}} \leq \eta^{\text{qm}}_\infty < \eta_C$ as well. □

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7.5.2. A MORE GENERAL FINAL BATTERY STATE

For the simplicity of our analysis, we have assumed that the battery is left in the specific final state described in Eq. (6.2.6), i.e. an amount of work $W_{\text{ext}} = E_k - E_j$ is extracted, except with failure probability ε that the battery remains in the initial state $|E_j\rangle\langle E_j|_{\text{W}}$. In this section, we show that this is a simplification which can be removed in general, i.e. the final battery state is allowed to be any state within the ε-ball of $|E_k\rangle\langle E_k|_{\text{W}}$. In particular, our result that the Carnot efficiency cannot be achieved when $\Omega > 1$ still holds.

Proof Sketch

In Lemma 7.17, we show that for any final state of the cold bath ρ^{1}_{Cold}, allowing a more general final battery state does not affect the amount of *work* bounded by the F_∞ condition, provided ε is upper bounded by a constant factor. We then use this to prove in Theorem 7.3 that for the case of near perfect work extraction, when $\Omega > 1$, η_C cannot be achieved even if we allow a more general battery final state.

Lemma 7.17. *For any given $\rho^{0}_{\text{Cold}}, \rho^{1}_{\text{Cold}}$, with $\rho^{0}_{\text{W}} = |E_j\rangle\langle E_j|_{\text{W}}$, consider the maximum $W^{1}_{\infty} := E_{k_1} - E_j$ such that $\rho^{0}_{\text{Cold}} \otimes \rho^{0}_{\text{W}} \to \rho^{1}_{\text{Cold}} \otimes \rho^{1}_{\text{W}}$ is allowed by the non-increasing F_∞ condition, which is equivalent to having*

$$D_\infty(\rho^{0}_{\text{Cold}} \| \tau^{\beta_h}_{\text{Cold}}) + D_\infty(\rho^{0}_{\text{W}} \| \tau^{\beta_h}_{\text{W}}) \geq D_\infty(\rho^{1}_{\text{Cold}} \| \tau^{\beta_h}_{\text{Cold}}) + D_\infty(\rho^{1}_{\text{W}} \| \tau^{\beta_h}_{\text{W}}), \tag{7.5.69}$$

with

$$\rho_{\mathrm{W}}^{1} = (1-\varepsilon)|E_{k_1}\rangle\langle E_{k_1}|_{\mathrm{W}} + \varepsilon|E_j\rangle\langle E_j|_{\mathrm{W}}. \tag{7.5.70}$$

On the other hand, consider any battery final state

$$\rho_{\mathrm{W}}^{2} = (1-\varepsilon)|E_{k_2}\rangle\langle E_{k_2}|_{\mathrm{W}} + \varepsilon\rho_{\mathrm{W}}^{\mathrm{junk}}, \tag{7.5.71}$$

where $\rho_{\mathrm{W}}^{\mathrm{junk}}$ *is an block-diagonal state orthogonal to* $|E_{k_2}\rangle\langle E_{k_2}|_{\mathrm{W}}$ *which may depend on* ε*, i.e.* $\rho_{\mathrm{W}}^{\mathrm{junk}} = \sum_i p_i|E_i\rangle\langle E_i|_{\mathrm{W}}$ *with* $p_{k_2} = 0$ *and* $\sum_i p_i = 1$*. Define* $W_\infty^2 := E_{k_2} - E_j$ *such that* $\rho_{\mathrm{Cold}}^{0} \otimes \rho_{\mathrm{W}}^{0} \to \rho_{\mathrm{Cold}}^{1} \otimes \rho_{\mathrm{W}}^{2}$ *is allowed by the non-increasing* F_∞ *condition, i.e.*

$$D_\infty(\rho_{\mathrm{Cold}}^{0}\|\tau_{\mathrm{Cold}}^{\beta_h}) + D_\infty(\rho_{\mathrm{W}}^{0}\|\tau_{\mathrm{W}}^{\beta_h}) \geq D_\infty(\rho_{\mathrm{Cold}}^{1}\|\tau_{\mathrm{Cold}}^{\beta_h}) + D_\infty(\rho_{\mathrm{W}}^{2}\|\tau_{\mathrm{W}}^{\beta_h}). \tag{7.5.72}$$

Then for all $0 < \varepsilon \leq \hat{\varepsilon} = \left[1 + e^{\beta_h(E_{\max} - E_j)}\right]^{-1}$*,* $E_{\max}$ *being the largest energy eigenvalue of* $\hat{H}_W$*, we have* $W_\infty^1 = W_\infty^2$*.*

Proof. Firstly, note that any block-diagonal state ρ_{W}^2 with trace distance $d(\rho_{\mathrm{W}}^2, |E_{k_2}\rangle\langle E_{k_2}|_{\mathrm{W}}) = \varepsilon$ can be written in the form of Eq. (7.5.71). Rearranging the terms in Eq. (7.5.69),

$$D_\infty(\rho_{\mathrm{W}}^{1}\|\tau_{\mathrm{W}}^{\beta_h}) \leq D_\infty(\rho_{\mathrm{W}}^{0}\|\tau_{\mathrm{W}}^{\beta_h}) + D_\infty(\rho_{\mathrm{Cold}}^{0}\|\tau_{\mathrm{Cold}}^{\beta_h}) - D_\infty(\rho_{\mathrm{Cold}}^{1}\|\tau_{\mathrm{Cold}}^{\beta_h}) =: A. \tag{7.5.73}$$

Using the definition of D_∞ in Eq. (2.3.4) to expand the L.H.S. of Eq. (7.5.73), we obtain

$$\ln\max\left\{(1-\varepsilon)e^{\beta_h E_{k_1}}\ ,\ \varepsilon e^{\beta_h E_j}\right\} \leq A - \ln Z_{\mathrm{W}}^{\beta_h}. \tag{7.5.74}$$

We know that since near perfect work is extracted, ε is arbitrarily small. This implies that for ε small enough, $\max\left\{(1-\varepsilon)e^{\beta_h E_{k_1}}\ ,\ \varepsilon e^{\beta_h E_j}\right\} = (1-\varepsilon)e^{\beta_h E_{k_1}}$.

Similarly, one can evaluate Eq. (7.5.69) to obtain

$$\ln\max\left\{(1-\varepsilon)e^{\beta_h E_{k_2}}\ ,\ \left\{\varepsilon p_i e^{\beta_h E_i}\right\}_{i\neq k_2}\right\} \leq A - \ln Z_{\mathrm{W}}^{\beta_h}. \tag{7.5.75}$$

Note that the maximization in Eq. (7.5.75) only picks out the maximum value. In particular, denoting $E_{\max}$ to be the largest energy eigenvalue of the battery, then whenever

$$(1-\varepsilon)e^{\beta_h E_{k_2}} \geq \varepsilon e^{\beta_h E_{\max}}, \tag{7.5.76}$$

or equivalently

$$\varepsilon \leq \left[1 + e^{\beta_h(E_{\max} - E_{k_2})}\right]^{-1}, \tag{7.5.77}$$

then $\max\left\{(1-\varepsilon)e^{\beta_h E_{k_2}}\ ,\ \left\{\varepsilon p_i e^{\beta_h E_i}\right\}_{i\neq k_2}\right\} = (1-\varepsilon)e^{\beta_h E_{k_2}}$. In other words, as long as ε is upper bounded by Eq. (7.5.77), we know which terms attains the maximization in Eq. (7.5.74). However, we also want an upper bound that is independent of any limit involving the final

state ρ^1_{ColdMW} we wish to take, or any amount of work extracted (and therefore, we want the bound to be independent of E_{k_2}). As such, let us construct the upper bound $\varepsilon \leq \hat{\varepsilon}$ where[8],

$$\hat{\varepsilon} := \inf_{\substack{E_{k_2} \\ W^2_\infty > 0}} \left[1 + e^{\beta_h (E_{\max} - E_{k_2})}\right]^{-1} = \left[1 + e^{\beta_h (E_{\max} - E_j)}\right]^{-1}. \tag{7.5.78}$$

Finally, note that for $\varepsilon \leq \hat{\varepsilon}$, E_{k_1} and E_{k_2} correspond to solutions for the maximization in both Eq. (7.5.74) and Eq. (7.5.75), and the R.H.S. are identical for both equations. Therefore, the maximum possible values for E_{k_1}, E_{k_2} are the same, and hence $W^1_\infty = W^2_\infty$. □

We will use Lemma 7.17 to prove Theorem 7.3. But before we proceed, let us fix some notation. Define the efficiency as a function of $\alpha \geq 0$:

$$\begin{aligned} \eta^J_\alpha(\rho^1_{\text{Cold}}) = \sup_{E_{k_J} - E_j > 0} \ & \eta(\rho^1_{\text{Cold}}) \\ \text{s.t.} \quad & F_\alpha(\rho^0_{\text{W}} \otimes \tau^0_{\text{Cold}}, \tau^h_{\text{ColdW}}) \geq F_\alpha(\rho^J_{\text{W}} \otimes \rho^1_{\text{Cold}}, \tau^h_{\text{ColdW}}), \\ & \text{tr}(\hat{H}_t \rho^0_{\text{ColdHotMW}}) = \text{tr}(\hat{H}_t \rho^{1,J}_{\text{ColdHotMW}}). \end{aligned}$$

with $J = 1, 2$ denotes the final battery ρ^J_{W}. We also define an α-independent efficiency:

$$\begin{aligned} \eta^J(\rho^1_{\text{Cold}}) = \sup_{E_{k_J} - E_j > 0} \ & \eta(\rho^1_{\text{Cold}}) \\ \text{s.t.} \quad & F_\alpha(\rho^0_{\text{W}} \otimes \tau^0_{\text{Cold}}, \tau^h_{\text{ColdW}}) \geq F_\alpha(\rho^J_{\text{W}} \otimes \rho^1_{\text{Cold}}, \tau^h_{\text{ColdW}}), \ \forall \alpha \geq 0. \end{aligned}$$

Note that for any $\alpha \geq 0$, and any state ρ^1_{Cold}, $\eta^J_\alpha(\rho^1_{\text{Cold}}) \geq \eta^J(\rho^1_{\text{Cold}})$ holds.

We already know from Theorem 7.1 that when $\Omega > 1$, for any final cold bath state ρ^1_{Cold}, the efficiency $\eta^1(\rho^1_{\text{Cold}}) < \eta_C$. Theorem 7.3 shows that this is also true for $\eta^2(\rho^1_{\text{Cold}})$, i.e. when allowing a more general battery final state.

Theorem 7.3. *Consider a heat engine with a cold bath consisting of n qubits, that extracts near perfect work. If $\Omega > 1$ as defined in Eq. (7.4.47), then for any final cold bath state ρ^1_{Cold}, the efficiency $\eta^2(\rho^1_{\text{Cold}})$ is strictly less than the Carnot efficiency.*

Proof. Firstly, suppose that $\Omega > 1$. By Lemma 7.10, we know that the maximum allowed amount of work is evaluated at $\alpha = \infty$, and by Lemma 7.11 we know that the efficiency for quasi-static heat engine is

$$\lim_{g \to 0} \eta^1(\tau_{\beta_f}) = \lim_{g \to 0} \eta^1_\infty(\tau_{\beta_f}) < \eta_C. \tag{7.5.79}$$

On the other hand, by Lemma 6.6, $\eta^2(\rho^1_{\text{Cold}})$ can only possibly achieve Carnot efficiency in the quasi-static limit. In other words, for all other final states ρ^1_{Cold} we know that Carnot efficiency cannot be achieved. It suffices to see that in the quasi-static limit,

$$\lim_{g \to 0} \eta^2(\tau_{\beta_f}) \leq \lim_{g \to 0} \eta^2_\infty(\tau_{\beta_f}) = \lim_{g \to 0} \eta^1_\infty(\tau_{\beta_f}) = \lim_{g \to 0} \eta^1(\tau_{\beta_f}) < \eta_C. \tag{7.5.80}$$

[8] Although such a bound is dependent on $\hat{H}_{\text{W}}$, note that as long as $\hat{H}_{\text{W}}$ has a finite-dimensional spectra, $\hat{\varepsilon}$ is a fixed value that does not vanish to zero, and does not exceed $\frac{1}{2}$.

The second equality is obtained by noting that for any state $\tilde{\rho}^1_{\text{Cold}}$ (and therefore for τ_{β_f}):

1. ΔC is the same for both expressions of efficiency $\eta^1_\infty(\rho^1_{\text{Cold}})$ and $\eta^2_\infty(\rho^1_{\text{Cold}})$.
2. For any heat engine that extracts near perfect work, only the limit $\varepsilon \to 0$ is relevant, and by Lemma 7.17, for all $0 < \varepsilon < \left[1 + e^{\beta_h(E_{\max} - E_j)}\right]^{-1}$, $W^1_\infty(\tilde{\rho}^1_{\text{Cold}}) = W^2_\infty(\tilde{\rho}^1_{\text{Cold}})$.

Hence, from Items 1 and 2, one concludes that $\eta^1_\infty(\tilde{\rho}^1_{\text{Cold}}) = \eta^2_\infty(\tilde{\rho}^1_{\text{Cold}})$ for any state $\tilde{\rho}^1_{\text{Cold}}$. The third equality in Eq. (7.5.80) comes directly from Eq. (7.5.79). □

7.6. EFFICIENCY OF DRAWING IMPERFECT WORK WITH ENTROPY COMPARABLE WITH W_{ext}

One can ask whether it is possible to exceed Carnot efficiency when imperfect work is extracted. In this section, we first consider a sub-regime of imperfect work, where

$$\frac{\Delta S}{W_{\text{ext}}} \to p \qquad \text{for some } p > 0. \tag{7.6.1}$$

One can see that only certain choices of $\varepsilon(g)$ will lead to having such a limit, which we have seen on Table 7.2. We prove that for all choices of ε such that Eq. (7.6.1) is true, one cannot surpass the Carnot efficiency. However, it is interesting to note that, if only the standard free energy is responsible for determining state transitions, then Carnot efficiency might be exceeded!

Theorem 7.4. *Consider a quasi-static heat engine where the failure probability of extracting work is $\varepsilon(g)$, g being the quasi-static parameter, such that*

$$\lim_{g\to 0^+} \frac{\varepsilon^\kappa(g)}{g} = \begin{cases} 0 & \text{if } \kappa \geq 1 \\ \infty & \text{if } \kappa < 1. \end{cases} \tag{7.6.2}$$

and $\lim_{g\to 0} \dfrac{\varepsilon \ln \frac{1}{\varepsilon}}{g} = c > 0$. *Then the maximum achievable efficiency is upper bounded by the Carnot efficiency.*

Proof. Firstly, note that an example for such a choice of ε can be constructed, i.e. $\varepsilon \ln \frac{1}{\varepsilon} = c \cdot g$.

We make use of Eq. (7.6.2) to analyze W_{ext}. Rewriting Eq. (7.3.51) by first drawing out a factor of g,

$$W_{\text{ext}} = g \cdot \inf_{\alpha > 0} \tilde{W}_\alpha, \tag{7.6.3}$$

where

$$\tilde{W}_\alpha = \begin{cases} \frac{1}{\beta_h(\alpha-1)}\left[\alpha n B_\alpha - \frac{\varepsilon^\alpha}{g} + \frac{\alpha\varepsilon}{g}\right] + \Theta(g) + \Theta\left(\frac{\varepsilon^{2\alpha}}{g}\right) + \Theta(\varepsilon^\alpha) + \Theta\left(\frac{\varepsilon^2}{g}\right), & \text{if } \alpha \in (0,\infty)\setminus\{1\}, \\ \beta_h^{-1}\left[\lim\limits_{\alpha\to 1^+} \dfrac{\alpha n B_\alpha}{\alpha - 1} + \dfrac{\varepsilon \ln \frac{1}{\varepsilon}}{g}\right] + \Theta(\varepsilon) + \Theta\left(\frac{\varepsilon^2 \ln \varepsilon}{g}\right) + \Theta\left(\frac{\varepsilon^2}{g}\right) + \Theta(g), & \alpha = 1. \end{cases} \tag{7.6.4}$$

Note that the (inverse) efficiency in the quasi-static limit is given by

$$\eta^{-1} = \lim_{g\to 0^+} 1-\varepsilon+\frac{\Delta C}{W_{\text{ext}}} = 1+\lim_{g\to 0^+}\frac{\Delta C}{W_{\text{ext}}} \geq 1+\lim_{g\to 0^+}\frac{\Delta C}{W_\alpha}, \tag{7.6.5}$$

where any $\alpha > 0$ gives an upper bound. However, since ΔC and W_α are both vanishing in the quasi-static limit (for any $\alpha > 0$), we can also evaluate the limit by using Eq. (7.3.30),

$$\lim_{g\to 0^+}\frac{\Delta C}{W_\alpha} = \frac{nB_1'}{\beta_c-\beta_h}\cdot\left(\lim_{g\to 0}\tilde{W}_\alpha\right)^{-1}. \tag{7.6.6}$$

We are, then, interested in picking α that gives us the tightest bound, i.e. the smallest value for $\lim_{g\to 0}\tilde{W}_\alpha$. This leads us to scrutinize Eq. (7.6.4) in the light of $\varepsilon(g)$ that satisfies the statement of the theorem. First of all, note that Eq. (7.6.2) implies that for values of $\alpha \in (0,1)$, the term $\frac{-\varepsilon^\alpha}{g(\alpha-1)}$ goes to infinity as $g\to 0^+$, while other terms are finite. This implies that the minimization can be restricted to parameters $\alpha \geq 1$. Notice also all the order terms vanish when we take the limit $g\to 0$, therefore we need only to deal with the largest order terms in Eq. (7.6.4).

Consider the case where $\alpha = 1$. We have that

$$\lim_{g\to 0}\tilde{W}_1 = \frac{1}{\beta_h}\left[\lim_{\alpha\to 1^+}\frac{\alpha n B_\alpha}{\alpha-1}+c\right], \tag{7.6.7}$$

where we have seen that $c > 0$, by choice of $\varepsilon(g)$. On the other hand, for $\alpha > 1$ the expression for $\tilde{W}_\alpha$ can be further simplified in the quasi-static limit,

$$\lim_{g\to 0}\tilde{W}_\alpha = \frac{\alpha n B_\alpha}{\beta_h(\alpha-1)} \qquad \text{if } \alpha\in(1,\infty). \tag{7.6.8}$$

This is because the terms $\frac{\varepsilon^\alpha}{g}, \frac{\alpha\varepsilon}{g}$ now vanish as $g\to 0^+$. From this we also see that since $\tilde{W}_1 > \beta_h^{-1}\lim_{\alpha\to 1^+}\frac{\alpha n B_\alpha}{\alpha-1}$, and by continuity of the function $\frac{\alpha n B_\alpha}{\alpha-1}$ for $\alpha\in(1,\infty)$, $\tilde{W}_1$ can also be disregarded in the minimization (see Figure 7.9 for a pictorial understanding).

Figure 7.9: The value of $\tilde{W}_\alpha$ at $\alpha = 1$ can be ignored while minimizing $\tilde{W}_\alpha$ over $\alpha\in[1,\infty)$, because the neighbouring values of the function for $\alpha > 1$ is lower.

Upon scrutiny, one sees that in the quasi-static limit, the contribution from ε has dropped out of the expression for W_{ext}. Intuitively this tells us that having such a probability of failure ε does not help to boost W_{ext}, and in turn the efficiency. In particular, we can use the lower bound:

$$\eta^{-1} = 1+\lim_{g\to 0^+}\frac{\Delta C}{W_{\text{ext}}} \geq \frac{nB_1'}{\beta_c-\beta_h}\left[\lim_{\alpha\to 1}\frac{\alpha n B_\alpha}{\beta_h(\alpha-1)}\right]^{-1}, \tag{7.6.9}$$

where we have substituted Eq. (7.6.8) and (7.6.6) into Eq. (7.6.5), while picking $\alpha\to 1$ as our bound. This limit is evaluated as

$$\lim_{\alpha\to 1^+}\frac{\alpha n B_\alpha}{\alpha-1} = \frac{n}{\beta_h}(B_1+B_1') = \frac{n}{\beta_h}B_1'. \tag{7.6.10}$$

The first equality in Eq. (7.6.10) comes by noting that $B_1 = 0$, and therefore applying the L'Hospital rule. The second equality comes again from noting that $B_1 = 0$. Finally, substituting this into Eq. (7.6.9), we have

$$\eta^{-1} \geq 1 + \frac{nB_1'}{\beta_c - \beta_h} \cdot \frac{\beta_h}{nB_1'} \tag{7.6.11}$$

$$= 1 + \frac{\beta_h}{\beta_c - \beta_h} = \eta_C^{-1}. \tag{7.6.12}$$

one finds that the upper bound on efficiency yields the Carnot expression, i.e. $\eta \leq \eta_C$. This means that for choices of $\varepsilon(g)$ according to the statement of the theorem, Carnot efficiency cannot be surpassed. □

Remark 7.1. *By comparing Eq.* (7.6.8) *and Eq.* (7.4.6)*, we see that this sub-regime of imperfect work is actually very similar to the case of near perfect work when* $\bar{\kappa} = 1$*. In particular, the value of* W_{ext} *is given over the same minimization, i.e. over values* $\alpha > 1$ *of the second laws, and the contributions from* ε *vanish in the quasi-static limit. Therefore, it follows that the results regarding achievability of Carnot efficiency (depending on bath Hamiltonian), such as Lemma 7.11 and Theorem 7.1, not only holds for near perfect work, but also for this sub-regime of imperfect work.*

In conclusion, in the regime where p is finite, the reason that one cannot exceed Carnot efficiency stems from the fact that there exists a continuous family of generalized free energies in the quantum microregime.

7.7. SURPASSING η_C WITH IMPERFECT WORK

7

In this section, we show that if one considers imperfect work, then heat contributions will allow us to surpass the Carnot efficiency. In this section, we will mainly be focusing on the case where $\hat{H}_{\text{Cold}}$ consists of n-identical qubits. We begin with a proof outline, followed by the technical lemmas developed in Section 7.7.1. The results are then summarized in Section 7.7.2.

Proof Sketch

Let us first recall certain results which we have previously derived, by restating them here for the reader's convenience. Applying the generalized second laws, by Lemma 7.3, W_{ext} is given by a minimization problem over the continuous range of a real-valued variable $\alpha > 0$,

$$W_{\text{ext}} = \inf_{\alpha > 0} W_\alpha, \tag{7.7.1}$$

where for $\alpha \in (0, \infty) \backslash \{1\}$,

$$W_\alpha = \frac{1}{\beta_h(\alpha - 1)} \left[\ln(A - \varepsilon^\alpha) - \alpha \ln(1 - \varepsilon) \right], \tag{7.7.2}$$

$$A = \left(\frac{\sum_i p_i^\alpha q_i^{1-\alpha}}{\sum_i p_i'^\alpha q_i^{1-\alpha}} \right)^n, \tag{7.7.3}$$

where $p_i = \frac{e^{-\beta_c E_i}}{Z_{\beta_c}}$ are the eigenvalues of the thermal state for $\hat{H}_c$ at inverse temperature β_c, p_i' are eigenvalues of the final cold bath ρ^1_{Cold}, and $q_i = \frac{e^{-\beta_h E_i}}{Z_{\beta_h}}$ are the probabilities corresponding to the thermal state of the cold bath with respect to β_h. The quantities W_1, W_∞ are defined by the limits $\lim_{\alpha\to 1} W_\alpha, \lim_{\alpha\to\infty} W_\alpha$ respectively.

Earlier in Eq. (7.3.51), we also showed that the expansion of W_α for any $\alpha > 0$, in the regime where $g, \varepsilon \to 0$ can be written as the following:

$$W_\alpha = \frac{1}{\beta_h(\alpha-1)}\left[\alpha n g B_\alpha - \varepsilon^\alpha + \alpha\varepsilon\right] + \Theta(g^2) + \Theta(\varepsilon^{2\alpha}) + \Theta(g\varepsilon^\alpha) + \Theta(\varepsilon^2), \tag{7.7.4}$$

and for $\alpha = 1$,

$$W_1 = \left[\lim_{\alpha\to 1^+} \frac{1}{\beta_h(\alpha-1)}\left(\alpha n g B_\alpha - \varepsilon^\alpha + \alpha\varepsilon\right)\right] + \Theta(\varepsilon g) + \Theta(\varepsilon^2 \ln\varepsilon) + \Theta(\varepsilon^2) + \Theta(g^2), \tag{7.7.5}$$

where the function ${B_\alpha}^a$, when $\hat{H}_{\text{Cold}}$ consists of n identical qubits with energy gap E, is given by

$$B_\alpha = \frac{E}{1+e^{\beta_c E}} \cdot \frac{e^{(\beta_h+\alpha\beta_c)E} - e^{(\beta_c+\alpha\beta_h)E}}{e^{\alpha\beta_h E} + e^{(\beta_h+\alpha\beta_c)E}} \tag{7.7.6}$$

Furthermore, we also checked explicitly that by first taking the limit $\lim_{\alpha\to\infty} W_\alpha$, then expanding in small g, ε gives the same expression, i.e. Eq. (7.7.4) holds also in the limit $\alpha \to \infty$.

Therefore, the difficulty of evaluating the efficiency lies in performing the optimization of W_α over $\alpha \in (0,\infty)$, which is neither monotonic nor convex. However, by manipulating our freedom of choosing ε, we show that in certain parameter regimes of β_c, β_h, and E, one can evaluate a simple, analytical expression for W_{ext}. The steps taken are outlined as follows:

1. We start by choosing the failure probability to be $\varepsilon = \varepsilon_1 \cdot g$, where ε_1 is independent of the quasi-static parameter g.

2. Starting out from the expression for extractable work given in Eq. (7.7.4) and (7.7.5), we prove that in the quasi-static limit, the regime $\alpha \in (0,1]$ need not be considered in the optimization. This is proven in Lemma 7.18.

3. We show that the function W_α which we desire to minimize has at most one unique local minima. To do so, we establish technical Lemmas 7.21, 7.22 and 7.23, in order to arrive at Lemma 7.24.

4. We show that ε_1 can be chosen such that $\varepsilon > 0$ (Lemma 7.25), and that we choose it so that we know that a particular $\alpha^* \in (1,2)$ corresponds to a stationary point (Lemma 7.26), specifically a local minima (Lemma 7.27). Since we established Item 3, this implies that we have identified a unique local minima.

5. We show that under certain conditions, $W_{\alpha^*} < W_\infty$. This implies that W_{α^*} corresponds to the global minima which we desire to evaluate.

6. The conditions for Items 3-5 are summarized in Corollary 7.2, where one can now, by choosing the parameter α^*, evaluate W_{ext} analytically, and therefore use

$$\eta^{-1} = 1 - \varepsilon + \frac{\Delta C}{W_{\text{ext}}} \tag{7.7.7}$$

to calculate the efficiency. On the other hand, the calculation of ΔC is straightforward once $\rho^0_{\text{Cold}}, \rho^1_{\text{Cold}}$ are fixed, and for the quasi-static limit, we expand ΔC in terms of the quasi-static parameter g.

[a] The function B_α was defined in Eq. (7.3.18), and reduces to a simplified expression for the case where the cold bath consists of n identical qubits in Eq. (7.4.28).

7.7.1. TECHNICAL LEMMAS USED FOR THE PROOF OF COROLLARY 7.2

Building on the results adapted Section 7.3, this section contains the technical lemmas and proofs used to develop the proof of Corollary 7.2.

Lemma 7.18. *Given any heat engine, consider the state transition*

$$\tau_{\beta_{\text{Cold}}} \otimes \rho^0_{\text{W}} \to \rho^1_{\text{Cold}} \otimes \rho^1_{\text{W}}, \tag{7.7.8}$$

where $\rho^0_{\text{W}} = |E_j\rangle\langle E_j|_{\text{W}}$, $\rho^1_{\text{W}} = (1-\varepsilon)|E_k\rangle\langle E_k|_{\text{W}} + \varepsilon|E_j\rangle\langle E_j|_{\text{W}}$ *respectively, where* $W_{\text{ext}} = E_k - E_j$. *Let* $\varepsilon = \varepsilon_1 \cdot g$, *where note that* $\varepsilon_1 > 0$ *is independent of* α *and* g. *Then there exists* $g' > 0$ *such that for all* $0 < g \leq g'$,

$$W_{\text{ext}} = \inf_{\alpha>0} W_\alpha = \inf_{\alpha>1} W_\alpha, \tag{7.7.9}$$

where W_α *is defined in Eq.* (7.7.4).

Proof. We start out from the most general expression of extractable work, given by Eq. (7.7.2). Let us first note that for any $\alpha \in [0,\infty)$, W_α is a continuous function of g, and that $\lim_{g\to 0} W_\alpha = 0$. This can be seen by directly plugging in $g = 0$ into Eq. (7.7.3), and since $\varepsilon = 0$, $|A|_{g=0} = 1$, therefore for all $\alpha > 0$, we have $W_\alpha = 0$ (the case of W_1 is automatically true as well, since W_1 is defined by taking the limit $\alpha \to 1$). Furthermore, for different values of $g > 0$, the value $W_{\text{ext}} = \inf_{\alpha>0} W_\alpha$ can be obtained at different values of α such that the optimal α depends on g. However, in the quasi-static limit, there must exist a particular $\alpha_1 > 0$ that achieves the minimum value, i.e.

$$\lim_{g\to 0} \frac{W_{\text{ext}}}{W_{\alpha_1}} = 1, \tag{7.7.10}$$

where This implies that for any $\alpha' \neq \alpha_1$, we have that

$$\lim_{g\to 0} \frac{W_{\alpha'}}{W_{\alpha_1}} \geq 1. \tag{7.7.11}$$

However, since we know that both $\lim_{g\to 0} W_{\alpha'} = 0$ and $\lim_{g\to 0} W_{\alpha_1} = 0$. Therefore by L'Hospital rule, this implies that if we define the first derivative of W_α w.r.t. g:

$$I(\alpha) = \frac{dW_\alpha}{dg}, \tag{7.7.12}$$

then for any α', we also have

$$\lim_{g\to 0} \frac{I(\alpha')}{I(\alpha_1)} \geq 1. \tag{7.7.13}$$

This implies that the solution α_1 to the minimization problem of $\inf_{\alpha>0} W_\alpha$, in the limit where $g \to 0$, is also the solution for the minimization problem $\inf_{\alpha>0} I(\alpha)$. Substituting $\varepsilon = \varepsilon_1 \cdot g$ into Eq. (7.7.12), we obtain

$$I(\alpha) = \frac{1}{\beta_h(\alpha-1)} \left[\frac{1}{A-\varepsilon^\alpha} \left(\frac{dA}{dg} - \alpha \varepsilon_1^\alpha g^{\alpha-1} \right) + \frac{\alpha \varepsilon_1}{1-\varepsilon} \right]. \tag{7.7.14}$$

We now see how Eq. (7.7.14) behaves when $g \to 0$. For any $\alpha < 1$, the terms involved are $A|_{g=0} = 1$, $\varepsilon|_{g=0} = 0$, $\left.\frac{dA}{dg}\right|_{g=0} = \alpha n B_\alpha$, and

$$g^{\alpha-1} \to \infty. \tag{7.7.15}$$

Eq. (7.7.15) in particular implies that in the limit of $g \to 0$, $I(\alpha)$ diverges to infinity in the interval $\alpha \in (0,1)$. Furthermore, note that since this does not happen for the regime $\alpha > 1$, and all other terms do not diverge, therefore in the $\alpha > 1$ regime there must be some α such that $I(\alpha) < \infty$ is finite. This allows us to conclude that $\alpha_1 \notin (0,1)$.

We will now exclude the point $\alpha = 1$ from the minimization. We make use of the small ε, g expansion of W_α in Eq. (7.7.4) to see why this is so, by calculating the limit $\lim_{g\to 0} \frac{W_1}{W_\infty}$. Let us first substitute $\varepsilon = \varepsilon_1 \cdot g$, and write out the expression for W_∞:

$$W_\infty = \lim_{\alpha\to\infty} W_\alpha = \frac{ng}{\beta_h} \left[\lim_{\alpha\to\infty} \frac{\alpha B_\alpha}{\alpha-1} + \frac{\varepsilon_1}{n} \right] + \Theta(g^2) + \Theta(\varepsilon^{2\alpha}) + \Theta(g\varepsilon^\alpha) + \Theta(\varepsilon^2) \tag{7.7.16}$$

$$= \frac{ng}{\beta_h} \left[B_\infty + \frac{\varepsilon_1}{n} \right] + \Theta(g^2), \tag{7.7.17}$$

where by definition of $\Theta(x)$ it is sufficient to keep the largest order term when several order functions are summed. One can check that $B_\infty = \lim_{\alpha\to\infty} B_\alpha$ is finite for all finite dimensional $\hat{H}_c$. Meanwhile, from Eq. (7.7.5), by substituting our choice of ε we have

$$W_1 = \frac{1}{\beta_h} \lim_{\alpha\to 1^+} \frac{\alpha n g B_\alpha - \varepsilon^\alpha + \alpha\varepsilon}{\alpha-1} + \Theta(\varepsilon g) + \Theta(\varepsilon^2 \ln\varepsilon) + \Theta(\varepsilon^2) + \Theta(g^2) \tag{7.7.18}$$

$$= \frac{1}{\beta_h} \lim_{\alpha\to 1^+} n g B'_\alpha + \alpha n g B_\alpha - \varepsilon^\alpha \ln\varepsilon + \varepsilon + \Theta(g^2 \ln g) \tag{7.7.19}$$

$$= \frac{ng}{\beta_h} \left[B'_1 - \varepsilon_1 \ln\varepsilon + \varepsilon_1 \right] + \Theta(g^2 \ln g) > \frac{ng}{\beta_h} \cdot \varepsilon_1 \cdot \ln\frac{1}{\varepsilon} + \Theta(g^2 \ln g). \tag{7.7.20}$$

The second equality comes by applying L'Hospital rule for differentiation limits, and the third equality comes by substituting $\alpha = 1$ into the equation, while noting that $B_1 = 0$, and

using $\varepsilon = \varepsilon_1 \cdot g$. The last inequality sign comes from noting that $B_1', \varepsilon_1 > 0$. Comparing Eq. (7.7.17) and (7.7.20) , we see that

$$\lim_{g\to 0} \frac{W_1}{W_\infty} > \lim_{g\to 0} \frac{\frac{ng}{\beta_h}\cdot \varepsilon_1 \cdot \ln\frac{1}{\varepsilon} + \Theta(g^2 \ln g)}{\frac{ng}{\beta_h}\left[B_\infty + \frac{\varepsilon_1}{n}\right] + \Theta(g^2)} = \lim_{g\to 0} \frac{\varepsilon_1 \cdot \ln\frac{1}{\varepsilon_1 \cdot g}}{B_\infty + \frac{\varepsilon_1}{n}} = \infty, \tag{7.7.21}$$

and therefore in the quasi-static regime, $W_1 > W_\infty$.

We have thus proven that in the quasi-static limit, the global minima for $W_{\text{ext}} = \inf_{\alpha>0} W_\alpha$ will not be obtained in the interval $\alpha \in (0, 1]$. This in turn implies that

$$\inf_{\alpha>0} W_\alpha = \inf_{\alpha>1} W_\alpha. \tag{7.7.22}$$

□

With Lemma 7.18, one can dismiss the regime $0 < \alpha \leq 1$ when considering the infimum over W_α in Eq. (7.7.4). Furthermore, we can already apply Lemma 7.18 to understand how $\frac{\Delta S}{W_{\text{ext}}}$ behaves in the quasi-static limit, which we prove in Lemma 7.19.

Lemma 7.19. *For any heat engine where $\varepsilon = \varepsilon_1 \cdot g$, with ε_1 independent of g, in the quasi-static limit $g \to 0^+$, we have*

$$\lim_{g\to 0^+} \frac{\Delta S}{W_{\text{ext}}} = \infty. \tag{7.7.23}$$

Proof. From Lemma 7.18, and by using Eq. (7.7.4) we see that for some particular $\alpha_1 \in (1, \infty)$,

$$W_{\text{ext}} = \frac{1}{\beta_h(\alpha_1 - 1)}\left[\alpha n g B_{\alpha_1} - \varepsilon^\alpha + \alpha\varepsilon\right] + \Theta(g^2) + \Theta(\varepsilon^{2\alpha}) + \Theta(g\varepsilon^\alpha) + \Theta(\varepsilon^2) \tag{7.7.24}$$

$$= \frac{g}{\beta_h(\alpha_1 - 1)}\left[\alpha_1 n B_{\alpha_1} + \alpha_1 \varepsilon_1\right] + \Theta(g^{\alpha_1}) + \Theta(g^2) + \Theta\left(g^{2\alpha_1}\right) + \Theta\left(g^{1+\alpha_1}\right). \tag{7.7.25}$$

This implies that the leading order term in W_{ext} is of first order in g. On the other hand,

$$\Delta S = -\varepsilon \ln\varepsilon - (1-\varepsilon)\ln(1-\varepsilon) \tag{7.7.26}$$

$$= -\varepsilon_1 \cdot g \ln(\varepsilon_1 \cdot g) - (1-\varepsilon)[-\varepsilon + \Theta(\varepsilon^2)] \tag{7.7.27}$$

$$= -\varepsilon_1 \cdot g \ln g + \varepsilon_1 \ln\varepsilon_1 \cdot g + \varepsilon + \Theta(\varepsilon^2) + \Theta(\varepsilon^3) \tag{7.7.28}$$

$$= -\varepsilon_1 \cdot g \ln g + \Theta(g) + \Theta(g^2) + \Theta(g^3). \tag{7.7.29}$$

The second equality is obtained by substituting $\varepsilon = \varepsilon_1 \cdot g$ and writing $\ln(1-\varepsilon) = -\varepsilon + \Theta(\varepsilon^2)$ in terms of Taylor expansion. The third equality is obtained by expanding out all the multiplied brackets, while the last equality is obtained by noting that $\Theta(\varepsilon) = \Theta(g)$, and therefore concluding that the leading order term (which has the slowest convergence rate as $g \to 0$) is of order $g \ln g$. With this, one can evaluate the limit

$$\lim_{g\to 0^+} \frac{\Delta S}{W_{\text{ext}}} = \lim_{g\to 0^+} \frac{-\varepsilon_1 \cdot g \ln g + \Theta(g) + \Theta(g^2) + \Theta(g^3)}{\frac{g}{\beta_h(\alpha_1-1)}\left[\alpha_1 n B_{\alpha_1} + \alpha_1\varepsilon_1\right] + \Theta(g^{\alpha_1}) + \Theta(g^2) + \Theta\left(g^{2\alpha_1}\right) + \Theta\left(g^{1+\alpha_1}\right)}$$

$$= \lim_{g\to 0^+} \frac{-\varepsilon_1 \cdot \ln g + \Theta(1) + \Theta(g) + \Theta(g^2)}{\frac{1}{\beta_h(\alpha_1-1)}\left[\alpha_1 n B_{\alpha_1} + \alpha_1\varepsilon_1\right] + \Theta(g^{\alpha_1-1}) + \Theta(g) + \Theta\left(g^{2\alpha_1-1}\right) + \Theta\left(g^{\alpha_1}\right)}$$

$$= \infty.$$

The second equality is obtained by dividing both numerator and denominator with g. Then we see that in the numerator, $-\varepsilon_1 \cdot \ln g$ goes to infinity, while the other terms remain finite. On the other hand, the denominator goes to a finite constant. Therefore, we conclude that $\lim_{g\to 0^+} \frac{\Delta S}{W_{\text{ext}}} = \infty$. □

In Lemma 7.18, we have also shown that in the quasi-static limit, the solution α_1 that corresponds to the infimum in W_{ext} coincides with the solution of the infimum for the function $I(\alpha) = \frac{dW_\alpha}{dg}$. By again making use of this function $I(\alpha)$, in the next step, we show that since we are interested in the quasi-static limit and the case where $\varepsilon = \varepsilon_1 \cdot g$, another useful simplification will help us to obtain the minimum for W_{ext}.

Lemma 7.20. *For $\varepsilon = \varepsilon_1 \cdot g$ where ε_1 is independent of α and g, consider the function*

$$I(\alpha) = \frac{dW_\alpha}{dg} = \frac{1}{\beta_h(\alpha-1)} \left[\frac{1}{A-\varepsilon^\alpha} \left(\frac{dA}{dg} - \alpha \varepsilon_1^\alpha g^{\alpha-1} \right) + \frac{\alpha \varepsilon_1}{1-\varepsilon} \right], \tag{7.7.30}$$

where W_α is given by Eqns. (7.7.2) *and* (7.7.3)*. Let α_1 be the solution that achieves the infimum in the quasi-static limit, such that for all other $\alpha' > 0$,*

$$\lim_{g\to 0} \frac{I(\alpha')}{I(\alpha_1)} \geq 1. \tag{7.7.31}$$

Then, α_1 is also the solution that achieves the infimum for $G(\alpha) = \frac{1}{\beta_h(\alpha-1)}(\alpha n B_\alpha + \alpha \varepsilon_1)$ in the regime $\alpha \in (1,\infty)$, i.e.

$$G(\alpha_1) = \inf_{\alpha>1} G(\alpha). \tag{7.7.32}$$

Proof. To see this, note that in Lemma 7.18 we have established that α_1 is not within the interval $(0,1]$, since within this interval, $\lim_{g\to 0} I(\alpha) = \infty$. On the other hand, for any $\alpha \in (1,\infty)$,

$$\lim_{g\to 0} I(\alpha) = \lim_{g\to 0} \frac{1}{\beta_h(\alpha-1)} \left[\frac{dA}{dg} - \alpha \varepsilon_1^\alpha g^{\alpha-1} + \alpha \varepsilon_1 \right] = G(\alpha). \tag{7.7.33}$$

This concludes the lemma. □

Lemma 7.20 implies that while analyzing $W_{\text{ext}} = \inf_{\alpha>0} W_\alpha$ in the quasi-static limit, where we are interested in finding the solution α_1 that satisfies Eq. (7.7.10), it suffices to analyze a much simpler function

$$G(\alpha) = \frac{1}{\beta(\alpha-1)}(\alpha n B_\alpha + \alpha \varepsilon_1), \tag{7.7.34}$$

since $G(\alpha_1) = \inf_{\alpha>1} G(\alpha)$. Looking back to compare $G(\alpha)$ with the Taylor expansion of W_α evaluated in Eq. (7.7.4), we see intuitively why this function provides us the same solution to α_1 as for W_{ext} in the quasi-static limit: $G(\alpha)$ is simply the largest order term (more precisely, it is the term associated with order g) of the Taylor expansion in the interval $\alpha \in (1,\infty)$.

$G(\alpha)$ HAS AT MOST ONE LOCAL MINIMA IN $\alpha \in (1,\infty)$

In this section, we prove a total of 4 lemmas, where the last Lemma 7.24 builds on the rest, arriving at the conclusion that $G(\alpha)$ has only at most one local minima in $\alpha \in (1,\infty)$.

The next Lemmas 7.21 and 7.22 would establish a useful property of $\frac{dG(\alpha)}{d\alpha}$, namely that this function has not more than 3 roots in the regime $\alpha \in (1,\infty)$, i.e. $G(\alpha)$ does not have more than 3 stationary points. Then in Lemma 7.23 we show how the value of $\lim_{\alpha\to\infty} G(\alpha)$ is approached. In the proof of these lemmas, we make use of the following quantities:

$$B'_\alpha = \frac{dB_\alpha}{d\alpha} = \frac{E^2(\beta_c-\beta_h)}{\left[e^{\alpha\beta_h E}+e^{(\beta_h+\alpha\beta_c)E}\right]^2}\cdot e^{[\beta_h+\alpha(\beta_c+\beta_h)]E} \tag{7.7.35}$$

$$B''_\alpha = \frac{d^2B_\alpha}{d\alpha^2} = \frac{E^3\left(\beta_c-\beta_h\right)^2}{\left[e^{\alpha\beta_h E}+e^{(\beta_h+\alpha\beta_c)E}\right]^3}\cdot e^{[\beta_h+\alpha(\beta_c+\beta_h)]E}\cdot\left[e^{\alpha\beta_h E}-e^{(\alpha\beta_c+\beta_h)E}\right]. \tag{7.7.36}$$

It is useful to note that whenever $\beta_c > \beta_h$, then for all $\alpha \geq 0$, $B'_\alpha > 0$ and $B''_\alpha < 0$.

In order to calculate the infimum of $G(\alpha)$ over the interval $\alpha > 1$, we compute

$$\frac{dG(\alpha)}{d\alpha} = \frac{n}{\beta_h}\frac{B'_\alpha}{(\alpha-1)^2}\left\{\alpha(\alpha-1)-\frac{B_\alpha}{B'_\alpha}-\frac{\varepsilon_1}{nB'_\alpha}\right\}. \tag{7.7.37}$$

Lemma 7.21. *Consider the function $f(\alpha) := \alpha(\alpha-1)-\frac{B_\alpha}{B'_\alpha}-\frac{\varepsilon_1}{nB'_\alpha}$, which is found in the R.H.S. of Eq. (7.7.37). Then its first derivative $f'(\alpha) = \frac{df(\alpha)}{d\alpha}$ is strictly concave in the domain $\alpha \in (1,\infty)$. This also implies that $f(\alpha)$ has at most 3 roots in the regime $\alpha \in (1,\infty)$.*

Proof. Note that $f'(\alpha) = g'(\alpha)+\frac{\varepsilon_1}{n}\frac{B''_\alpha}{B'^2_\alpha}$, where $g'(\alpha) = \frac{d}{d\alpha}\left[\alpha(\alpha-1)-\frac{B_\alpha}{B'_\alpha}\right]$. We have seen the exact same function before in Eq. (7.4.36) of Lemma 7.8, where we have shown that $g'(\alpha)$ is a strictly concave function. On the other hand, by using the definitions in Eq. (7.7.35) and (7.7.36), one can evaluate the second derivative of

$$\frac{d^2}{d\alpha^2}\frac{B''_\alpha}{B'^2_\alpha} = \left(\beta_c-\beta_h\right)^2 e^{-[\beta_h+\alpha(\beta_c+\beta_h)]E}E\cdot\left[e^{2\alpha\beta_h E}-e^{2(\alpha\beta_c+\beta_h)E}\right].$$

All the terms in the equation above are positive, except for the last term which is always negative in the regime $\alpha \in (1,\infty)$ when $\beta_h < \beta_c$. Therefore, the function $\frac{B''_\alpha}{B'^2_\alpha}$ is strictly concave as well. This implies that $f'(\alpha)$ is the addition of two strictly concave functions, and therefore is also strictly concave itself over the interval $\alpha \in (1,\infty)$. □

One can apply Lemma 7.21 to analyze the function $G(\alpha)$ to show that it does not have more than 3 stationary points.

Lemma 7.22 ($G(\alpha)$ has not more than 3 stationary points)**.** *Consider the continuous function $G(\alpha) = \frac{n}{\beta_h(\alpha-1)}\left[\alpha B_\alpha+\frac{\alpha\varepsilon_1}{n}\right]$ in the regime $\alpha \in (1,\infty)$. Then the equation $\frac{dG(\alpha)}{d\alpha} = 0$ has at most 3 roots, i.e. the function $G(\alpha)$ has not more than 3 stationary points.*

Proof. Let us begin by writing out the function

$$\frac{dG(\alpha)}{d\alpha} = \frac{n}{\beta_h}\frac{1}{(\alpha-1)^2}B'_\alpha\left[\alpha(\alpha-1)-n\frac{B_\alpha}{B'_\alpha}-\frac{\varepsilon_1}{nB'_\alpha}\right].$$

Since from the expression in Eq. (7.7.35), we see that $B'_\alpha > 0$ whenever $\beta_h < \beta_c$, by Lemma 7.21, we know that $\frac{dG(\alpha)}{d\alpha}$ can have at most 3 roots. □

Lemma 7.23 ($G(\alpha)$ is approached from above)**.** *Consider the continuous function* $G(\alpha) = \frac{n}{\beta_h(\alpha-1)}\left[\alpha B_\alpha + \frac{\alpha\varepsilon_1}{n}\right]$ *in the regime* $\alpha \in (1,\infty)$*. Then the limit* $\lim_{\alpha\to\infty} G(\alpha)$ *exists and is approached from above.*

Proof. We have seen from Eq. (7.7.17) that $\lim_{\alpha\to\infty} G(\alpha)$ exists and is some finite number. We then only need to prove that in the limit of large α, the quantity $\frac{dG(\alpha)}{d\alpha} < 0$. This can be seen from Eq. (7.7.37), which we rewrite here again

$$\frac{dG(\alpha)}{d\alpha} = \frac{n}{\beta_h}\frac{1}{(\alpha-1)^2}\left[\alpha(\alpha-1)B'_\alpha - B_\alpha - \frac{\varepsilon_1}{n}\right]. \tag{7.7.38}$$

Let us compare the terms in the large bracket of the R.H.S.. The first term

$$\alpha(\alpha-1)B'_\alpha = \alpha(\alpha-1)E^2(\beta_c-\beta_h)e^{-\beta_h E}e^{-\alpha(\beta_c-\beta_h)E} \tag{7.7.39}$$

has a quadratic term in α multiplied by a term which decreases exponentially in α, i.e. $\lim_{\alpha\to\infty}\alpha(\alpha-1)B'_\alpha = 0$. On the other hand, the remaining terms

$$\lim_{\alpha\to\infty} -B_\alpha - \frac{\varepsilon_1}{n} = -\left[\frac{E}{1+e^{\beta_c E}} + \frac{\varepsilon_1}{n}\right] < 0. \tag{7.7.40}$$

Since for large $\alpha \gg 1$, the multiplicative factor in Eq. (7.7.38) is positive, we have that $\frac{dG(\alpha)}{d\alpha} < 0$. This implies that the function $G(\alpha)$ approaches the limit $\alpha\to\infty$ from above. □

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Lemmas 7.22 and 7.23 combined gives us the next lemma, which further narrows down the amount of distinct local minimas for $G(\alpha)$ in the regime $\alpha \in (1,\infty)$.

Lemma 7.24. *The function* $G(\alpha)$ *has at most one local minima in the interval* $\alpha \in (1,\infty)$.

Proof. By Lemma 7.22, we know that the function $G(\alpha)$ has at most 3 stationary points in the regime $\alpha \in (1,\infty)$. Firstly, suppose that $G(\alpha)$ has only 1 or 2 stationary points. Then it is clear that there cannot exist two distinct local minimas, since for a continuous function with two local minimas, there has to be at least another local maxima in between, which is also a stationary point, which leads to a contradiction.

Now, suppose that $G(\alpha)$ has 3 stationary points, found at $1 < \alpha_1 < \alpha_2 < \alpha_3 < \infty$ respectively. Note that two neighbouring stationary points cannot both correspond to local minimas, as reasoned out in the previous paragraph. Therefore, the only way for there to exist 2 local minimum points, is to have α_1, α_3 corresponding to local minimas. If there are no more stationary points in the regime $\alpha > \alpha_3$, then $G(\alpha)$ can only be non-decreasing in $\alpha \in (\alpha_3,\infty)$, and the limit $\alpha\to\infty$ has to be approached from below. However, by Lemma 7.23 we know that this cannot be true.

This establishes the fact that $G(\alpha)$ does not have two distinct local minimas. Therefore, it implies that whenever we find some α^* corresponding to a local minima, it will be the unique *local* minima of the entire function. This simplifies the minimization of $G(\alpha)$ in Eq. (7.7.34) to comparing $G(\alpha^*)$ with $G(\infty)$.

□

INFIMUM FOR $G(\alpha)$ DETERMINED BY CHOICE OF ε_1

In the next 4 lemmas, we then prove that by making use of our liberty to choose ε_1, we can design it such that $\inf_{\alpha>1} G(\alpha)$ is obtained at any α^* we desire.

Lemma 7.25. *(Conditions for positive ε_1) Consider the function*

$$\varepsilon_1(a,n) := n[a(a-1)B'_a - B_a], \tag{7.7.41}$$

where $a \in \mathbb{R}, n \in \mathbb{Z}^+$. When the condition

$$E < \frac{2}{\beta_c - \beta_h} \frac{1+e^{\beta_c E}}{e^{\beta_c E}-1} \tag{7.7.42}$$

holds, then there exists some $\alpha^* > 1$ such that $\varepsilon_1(\alpha^*, n) > 0$.

Proof. We begin by noting that $\varepsilon(1,n) = 0$ for any $n \in \mathbb{Z}^+$. A Taylor expansion around $a = 1$ determines the positivity of $\varepsilon(a,n)$ for $a = 1+\delta$ where $\delta \ll 1$. Therefore, we calculate

$$\frac{d\varepsilon_1(a,n)}{da} = n[(a-1)B'_a + aB'_a + a(a-1)B''_a - B'_a] = n(a-1)[2B'_a + aB''_a]. \tag{7.7.43}$$

It is easy to see from Eq. (7.7.43) that $\frac{d\varepsilon_1(a,n)}{da}\Big|_{a=1} = 0$. Therefore, the term that determines positivity of $\varepsilon_1(a,n)$ around $a = 1$ is the second derivative,

$$\frac{d^2\varepsilon_1(a,n)}{da^2} = n[2B'_a + aB''_a + (a-1)(2B''_a + B''_a + aB'''_a)]. \tag{7.7.44}$$

The quantity $\frac{d^2\varepsilon_1(a,n)}{da^2}\Big|_{a=1} = n[2B'_1 + B''_1]$ we can expressed in a simplified form,

$$\frac{d^2\varepsilon_1(a,n)}{da^2}\Big|_{a=1} = \frac{n(\beta_c-\beta_h)e^{(\beta_c+3\beta_h)E}E^2}{[e^{\beta_h E}+e^{(\beta_c+\beta_h)E}]^3}\left[2+(\beta_c-\beta_h)E + e^{\beta_c E}(2-\beta_c E+\beta_h E)\right]. \tag{7.7.45}$$

For this to be positive, it implies that $2+(\beta_c-\beta_h)E + e^{\beta_c E}(2-\beta_c E+\beta_h E) > 0$. By further rearranging terms, we find

$$(\beta_c-\beta_h)E(1-e^{\beta_c E}) > -2(1+e^{\beta_c E}) \tag{7.7.46}$$

$$E < \frac{2}{\beta_c-\beta_h}\frac{e^{\beta_c E}+1}{e^{\beta_c E}-1}. \tag{7.7.47}$$

□

Lemma 7.26. *Consider the function $G(\alpha)$ as described in Eq. (7.7.34). When ε_1 is given by Eq. (7.7.41) for some $a = \alpha^* > 1$, then $\frac{dG(\alpha)}{d\alpha}\Big|_{\alpha=\alpha^*} = 0$.*

Proof. To see this, let us write out the final form of the first derivative of $G(\alpha)$ in Eq. (7.7.37),

$$\frac{dG(\alpha)}{d\alpha} = \frac{1}{\beta_h}\frac{1}{(\alpha-1)^2}\left\{\alpha(\alpha-1)nB'_\alpha - nB_\alpha - \varepsilon_1\right\}. \tag{7.7.48}$$

Substituting Eq. (7.7.41) into the equation above gives us 0 when $\alpha = \alpha^*$. □

So far, for a specific design of ε_1, we've found conditions expressed in Eq. (7.7.42) such that $\varepsilon_1 > 0$ and $G(\alpha^*)$ is a stationary point. Next, we can write down further conditions such that when given α^* and $\varepsilon_1(\alpha^*, n)$ as defined in Lemma 7.25, one can now find conditions on E such that $G(\alpha)$ not only is a stationary point, but also a local minima.

Lemma 7.27. *Consider the functions*

$$\frac{dG(\alpha)}{d\alpha} = \frac{1}{\beta_h}\frac{1}{(\alpha-1)^2}\left[\alpha(\alpha-1)nB'_\alpha - nB_\alpha - \varepsilon_1\right], \tag{7.7.49}$$

and

$$B_\alpha = \frac{E}{1+e^{\beta_c E}} \cdot \frac{e^{(\beta_h+\alpha\beta_c)E} - e^{(\beta_c+\alpha\beta_h)E}}{e^{\alpha\beta_h E} + e^{(\beta_h+\alpha\beta_c)E}}.$$

If the following condition holds:

$$E < \frac{1}{\beta_c - \beta_h}, \tag{7.7.50}$$

there one can find some $\alpha^* > 1$ in the vicinity of $\alpha = 1$ such that when we define $\varepsilon_1(\alpha^*, n) := n[\alpha^*(\alpha^*-1)B'_{\alpha^*} - B_{\alpha^*}]$, then $\varepsilon_1(\alpha^*, n) > 0$. Furthermore if $1 < \alpha^* < 2$ is chosen, then

$$\left.\frac{d^2G(\alpha)}{d\alpha^2}\right|_{\alpha=\alpha^*} > 0.$$

Proof. We first note that if $E < \frac{1}{\beta_c-\beta_h}$, then Eq. (7.7.42) holds and therefore by Lemma 7.25, one can choose $\alpha^* > 1$ and close to 1 such that $\varepsilon_1(\alpha^*, n) > 0$. Next, we calculate the analytical expression of $\frac{d^2G(\alpha)}{d\alpha^2}$ in terms of B'_α and B''_α. Differentiating Eq. (7.7.49),

$$\begin{aligned}
\frac{d^2G(\alpha)}{d\alpha^2} &= \frac{1}{\beta_h}\frac{1}{(\alpha-1)^4}\left\{(\alpha-1)^2\left[(\alpha-1)nB'_\alpha + \alpha nB'_\alpha + \alpha(\alpha-1)nB''_\alpha - nB'_\alpha\right]\right. \\
&\qquad \left. - 2(\alpha-1)\left[\alpha(\alpha-1)nB'_\alpha - nB_\alpha - \varepsilon_1\right]\right\} \\
&= \frac{1}{\beta_h}\frac{1}{(\alpha-1)^3}\left\{(\alpha-1)\left[2(\alpha-1)nB'_\alpha + \alpha(\alpha-1)nB''_\alpha\right] - 2\left[\alpha(\alpha-1)nB'_\alpha - nB_\alpha - \varepsilon_1\right]\right\} \\
&= \frac{1}{\beta_h}\frac{1}{(\alpha-1)^3}\left\{n(\alpha-1)^2\left[2B'_\alpha + \alpha B''_\alpha\right] - 2\left[\alpha(\alpha-1)nB'_\alpha - nB_\alpha - \varepsilon_1\right]\right\}.
\end{aligned} \tag{7.7.51}$$

Substituting $\alpha = \alpha^*$ into Eq. (7.7.51), one sees that the last term vanishes, and therefore

$$\left.\frac{d^2G(\alpha)}{d\alpha^2}\right|_{\alpha=\alpha^*} = \frac{n}{\beta_h}\frac{1}{(\alpha^*-1)}\left[2B'_{\alpha^*} + \alpha B''_{\alpha^*}\right]. \tag{7.7.52}$$

Since $\alpha^* > 1$, we see that to guarantee positivity of Eq. (7.7.52) is equivalent to showing that the last term $2B'_{\alpha^*} + \alpha B''_{\alpha^*}$ is strictly positive. To do so, we evaluate the terms B'_α and B''_α. By both hand derivation and Mathematica, we obtain the expressions

$$B'_\alpha = \frac{1}{[e^{\alpha\beta_h E} + e^{(\beta_h+\alpha\beta_c)E}]^2} \cdot E^2(\beta_c - \beta_h) \cdot e^{[\beta_h+\alpha(\beta_c+\beta_h)]E} \tag{7.7.53}$$

and

$$B''_\alpha = \frac{1}{[e^{\alpha\beta_h E} + e^{(\beta_h+\alpha\beta_c)E}]^3} \cdot E^3(\beta_c-\beta_h)^2 \cdot e^{[\beta_h+\alpha(\beta_c+\beta_h)]E} \cdot \left[e^{\alpha\beta_h E} - e^{(\alpha\beta_c+\beta_h)E}\right]. \quad (7.7.54)$$

One can then calculate the last term in Eq. (7.7.52), which we again obtain a simplified expression via Mathematica,

$$2B'_{\alpha^*} + \alpha B''_{\alpha^*} = \underbrace{\frac{(\beta_c-\beta_h)E^2}{[e^{\alpha\beta_h E} + e^{(\beta_h+\alpha\beta_c)E}]^3}}_{>0} \cdot \underbrace{e^{[\beta_h+\alpha(\beta_c+\beta_h)]E}}_{>0} \cdot f(\alpha^*), \quad (7.7.55)$$

where

$$f(\alpha^*) := e^{\alpha^*\beta_h E}[2+\alpha^*(\beta_c-\beta_h)E] + e^{(\alpha^*\beta_c+\beta_h)E}[2-\alpha^*(\beta_c-\beta_h)E] \quad (7.7.56)$$

$$= \underbrace{2\left[e^{\alpha^*\beta_h E} + e^{(\alpha^*\beta_c+\beta_h)E}\right]}_{>0} + \underbrace{\alpha^*(\beta_c-\beta_h)E\left[e^{\alpha^*\beta_h E} - e^{(\alpha^*\beta_c+\beta_h)E}\right]}_{<0}. \quad (7.7.57)$$

Note that the second term is always negative because $\alpha^* > 1$ and $\beta_c > \beta_h$. Therefore, to lower bound $f(\alpha^*)$ we want to upper bound the factor $\alpha^*(\beta_c-\beta_h)E$. By letting $1 < \alpha^* < 2$ and $E < \frac{1}{\beta_c-\beta_h}$, one can have $\alpha^*(\beta_c-\beta_h)E < 2$, which gives

$$2B'_{\alpha^*} + \alpha B''_{\alpha^*} > 2\left[e^{\alpha^*\beta_h E} + e^{(\alpha^*\beta_c+\beta_h)E}\right] + 2\left[e^{\alpha^*\beta_h E} - e^{(\alpha^*\beta_c+\beta_h)E}\right] = 4e^{\alpha^*\beta_h E} > 0. \quad (7.7.58)$$

Note that the constraints on α^* and E are not necessary, however sufficient and takes a relatively simple form. □

Finally, for $G(\alpha^*)$ to be the global minima, we need one last condition: that $G(\alpha^*) < G(\infty)$. In the next lemma, we again develop conditions such that this is true.

Lemma 7.28. *Suppose $\alpha^* E < \frac{1}{\beta_c-\beta_h}$. Then for $\varepsilon_1(\alpha^*, n)$ defined as in Eq. (7.7.41), we have that $G(\alpha^*) < G(\infty)$.*

Proof. To do so, we write out the expressions for $G(\alpha^*)$ and $G(\infty)$, while substituting in the expression for ε_1 in Eq. (7.7.41). The former can be written using Eq. (7.7.34), while the later has been derived in Eq. (7.7.17):

$$G(\alpha^*) = \frac{n}{\beta_h}\frac{\alpha^*}{\alpha^*-1}[B_{\alpha^*} + \alpha^*(\alpha^*-1)B'_{\alpha^*} - B_{\alpha^*}] = \frac{n}{\beta_h}\alpha^{*2}B'_{\alpha^*} \quad (7.7.59)$$

$$G(\infty) = \frac{n}{\beta_h}\left[\frac{E}{1+e^{\beta_c E}} + \frac{\varepsilon_1}{n}\right]. \quad (7.7.60)$$

For $G(\alpha^*) < G(\infty)$, this means

$$\alpha^{*2}B'_{\alpha^*} < \frac{E}{1+e^{\beta_c E}} + \alpha^*(\alpha^*-1)B'_{\alpha^*} - B_{\alpha^*},$$

and therefore

$$\frac{E}{1+e^{\beta_c E}} - \alpha^* B'_{\alpha^*} - B_{\alpha^*} > 0. \tag{7.7.61}$$

Expanding Eq. (7.7.61), and using the shorthand $X := e^{\alpha^*\beta_h E} + e^{(\beta_h+\alpha^*\beta_c)E}$, we obtain

$$\begin{aligned}
&\frac{E}{1+e^{\beta_c E}} - \frac{(\beta_c-\beta_h)\alpha^{*2}E^2}{X^2} e^{[\beta_h+\alpha^*(\beta_c+\beta_h)]E} - \frac{E}{1+e^{\beta_c E}} \frac{e^{(\beta_h+\alpha^*\beta_c)E} + e^{(\beta_c+\alpha^*\beta_h)E}}{X} \\
&= \frac{E}{1+e^{\beta_c E}} \frac{1}{X^2} \left\{ X^2 - \alpha^* E(\beta_c-\beta_h)(1+e^{\beta_c E}) e^{[\beta_h+\alpha^*(\beta_c+\beta_h)]E} - X\left[e^{\alpha^*\beta_h E} + e^{(\beta_h+\alpha^*\beta_c)E} \right] \right\} \\
&= \frac{E}{1+e^{\beta_c E}} \frac{1}{X^2} \left\{ X\left[e^{\alpha^*\beta_h E} + E^{(\alpha^*\beta_h+\beta_c)E} \right] - \alpha^* E(\beta_c-\beta_h)\left(1+e^{\beta_c E}\right) e^{[\beta_h+\alpha^* E(\beta_c+\beta_h)]E} \right\} \\
&= \frac{E}{X^2} \left\{ X e^{\alpha^*\beta_h E} - \alpha^* E\left(\beta_c-\beta_h\right) e^{[\beta_h+\alpha^* E(\beta_c+\beta_h)]E} \right\} \\
&= \frac{E}{X^2} \cdot e^{\alpha^*\beta_h E} \left\{ X - \alpha^* E\left(\beta_c+\beta_h\right) e^{(\beta_h+\alpha^*\beta_c)E} \right\} \\
&= \frac{E}{X^2} \cdot e^{\alpha^*\beta_h E} \left\{ e^{\alpha^*\beta_h E} + e^{(\beta_h+\alpha^*\beta_c)E} \left[1 - \alpha^* E\left(\beta_c-\beta_h\right) \right] \right\}.
\end{aligned}$$

The calculation above can be checked as follows: the first equality is obtained by taking out a common factor from all the three terms. The second equality focuses on the large bracket, and combines the first and third terms by expanding one of the X in the first term. In the third and fourth equality, one recognizes more common factors in the third line, and therefore pulls out the terms $e^{\alpha^*\beta_h E}$ and $(1+e^{\beta_c E})$. The fifth equality is obtained by expanding X, while regrouping terms. To demand that $W_{\alpha^*} < W_\infty$, implies that we want

$$e^{\alpha^*\beta_h E} + e^{(\beta_h+\alpha^*\beta_c)E} \left[1 - \alpha^* E(\beta_c-\beta_h) \right] > 0. \tag{7.7.62}$$

Rearranging Eq. (7.7.62), we have

$$e^{\alpha^*\beta_h E} > e^{(\beta_h+\alpha^*\beta_c)E} \left[\alpha^* E(\beta_c-\beta_h) - 1 \right]. \tag{7.7.63}$$

One can continue to simplify the expression by bringing $e^{(\beta_h+\alpha^*\beta_c)E}$, and subsequently the -1 to the L.H.S., yielding

$$1 + e^{-\alpha^*(\beta_c-\beta_h)E} e^{-\beta_h E} > \alpha^* E(\beta_c-\beta_h). \tag{7.7.64}$$

Since $\beta_c - \beta_h > 0$, one obtains an expression for $\alpha^* E$:

$$\alpha^* E < \frac{1 + e^{-\alpha^*(\beta_c-\beta_h)E} e^{-\beta_h E}}{\beta_c-\beta_h}. \tag{7.7.65}$$

Also, because $\beta_c - \beta_h > 0$, and we have that $e^{-\alpha^*(\beta_c-\beta_h)E} e^{-\beta_h E} > 0$, therefore as long as $\alpha^* E < \frac{1}{\beta_c-\beta_h}$, Eq. (7.7.61) is satisfied and $W_{\alpha^*} < W_\infty$. This concludes our proof. □

Lemma 7.18, 7.24, 7.25, 7.26 and 7.27 together presents a set of mathematical conditions such that α^* can be chosen such that W_α has a *global* minima at W_{α^*}. This is presented in Eq. (7.7.67) of Corollary 7.2.

7.7.2. EXAMPLES OF SURPASSING THE CARNOT EFFICIENCY

We conclude Section 7.7 by presenting Corollary 7.2, which formally states the main result of this section. It establishes a simplification of the efficiency of a quasi-static quantum heat engine, given a cold bath consisting of n identical qubits, each with energy gap E. In this corollary, we consider the special case where the failure probability $\varepsilon \propto g$ is proportional to the quasi-static parameter g, and evaluate the efficiency in the limit $g \to 0$. We have shown in Lemma 7.19 that this corresponds to extracting imperfect work, in particular, $\lim_{\varepsilon\to 0} \frac{\Delta S}{W_{\text{ext}}} = \infty$. For such a case, we show that whenever $E < \frac{1}{2(\beta_c-\beta_h)}$, then for some parameter α^*, we can choose the proportionality constant $c(\alpha^*) = \frac{\varepsilon}{g}$ such that the corresponding efficiency of such a heat engine is given by a simple analytical expression. Therefore, by numerically evaluating such an expression for different parameters $\beta_c, \beta_h, E, n, \alpha^*$ etc, one can find examples of surpassing the Carnot efficiency.

Corollary 7.2. *Consider a quasi-static heat engine with a cold bath consisting of n identical qubits with energy gap E. Given the inverse temperatures of the hot and cold bath $\beta_h, \beta_c > 0$ respectively, and for $\alpha \in (1,\infty)$ define the functions*

$$B_\alpha = \frac{E}{1+e^{\beta_c E}} \cdot \frac{e^{(\beta_h+\alpha\beta_c)E} - e^{(\beta_c+\alpha\beta_h)E}}{e^{\alpha\beta_h E} + e^{(\beta_h+\alpha\beta_c)E}}. \tag{7.7.66}$$

If the energy gap of the qubits satisfies

$$E < \frac{1}{2(\beta_c - \beta_h)}, \tag{7.7.67}$$

then there exists an $\alpha^* \in (1,2)$ such that the following holds:

1. *The failure probability of the heat engine, can be chosen as $\varepsilon = g \cdot n[\alpha^*(\alpha^*-1)B'_{\alpha^*} - B_{\alpha^*}] > 0$, where $B'_\alpha = \frac{dB_\alpha}{d\alpha}$ is the first derivative of B_α according to α.*
2. *In the quasi-static limit, the amount of extractable work W_{ext} is achieved by W_{α^*}, i.e.*

$$\lim_{g\to 0} \frac{W_{\text{ext}}}{W_{\alpha^*}} = 1. \tag{7.7.68}$$

3. *The (inverse) efficiency of the described heat engine in the quasi-static limit is given by $\eta^{-1} = 1 + \frac{\beta_h}{\beta_c-\beta_h} \frac{1}{\alpha^{*2}} \frac{B'_1}{B'_{\alpha^*}}$.*

Proof. Since $\frac{1+e^{\beta_c E}}{e^{\beta_c E}-1} > 1$, if Eq. (7.7.67) holds, then Eq. (7.7.42) holds. Therefore Item 1 is a direct result of Lemma 7.25.

Item 2 concerns the quantity W_{ext}, given by Eq. (7.7.1)-(7.7.3). Suppose that α_1 is the solution such that Eq. (7.7.68) holds. Since we have made a choice of ε according to Item (1), then in the proof of Lemma 7.18, we have shown that α_1 is also the solution that provides the infimum for

$$I(\alpha) = \frac{dW_\alpha}{dg} \tag{7.7.69}$$

in the quasi-static limit. Furthermore, in Lemma 7.20, we have also shown that α_1 is also the solution that ahieves the minimum for $\inf_{\alpha>1} G(\alpha)$, where $G(\alpha)$ is given by Eq. (7.7.34) (it is the leading order term of $I(\alpha)$ with respect to g). Therefore, if we can show that α^* achieves the global minima for $G(\alpha)$ in the region $\alpha \in (1,\infty)$, then we know that W_{α^*} satisfies Eq. (7.7.68).

Let us now see why the infimum $\inf_{\alpha>1} G(\alpha) = G(\alpha^*)$. If one chooses $\alpha^* \in (1,2)$ and that Eq. (7.7.67) holds, then Eq. (7.7.50) holds as well, and so Lemma 7.27 and Lemma 7.28. Therefore,

- By Lemma 7.24 we know $G(\alpha)$ does not have more than one distinct local minima.
- By Lemma 7.26 and 7.27, $G(\alpha^*)$ is a unique local minima.
- By Lemma 7.28, $G(\alpha^*) < G(\infty)$. Therefore, $G(\alpha^*)$ is the global minima.

Finally, for the fixed parameters $n \in \mathbb{Z}^+, E \in \mathbb{R}, \alpha^* \in (1,2)$, we can evaluate the efficiency of our quasi-static heat engine for a cold bath comprising of identical qubits. This can be done by evaluating the efficiency for our heat engine:

$$\eta^{-1} = \lim_{g\to 0^+} 1 - \varepsilon + \frac{\Delta C}{W_{\text{ext}}}. \tag{7.7.70}$$

The term $\varepsilon = \varepsilon_1 \cdot g = \Theta(g)$, where $\varepsilon_1 = n[\alpha^*(\alpha^*-1)B'_{\alpha^*} - B_{\alpha^*}]$ is a finite constant. Therefore we know $\lim_{g\to 0^+} \varepsilon = 0$. On the other hand, we have

$$\lim_{g\to 0} \frac{\Delta C}{W_{\text{ext}}} = \lim_{g\to 0} \frac{\Delta C}{W_{\text{ext}}} \cdot \frac{W_{\text{ext}}}{W_{\alpha^*}} = \lim_{g\to 0} \frac{\frac{d\Delta C}{dg}}{\frac{dW^*_\alpha}{dg}} \tag{7.7.71}$$

$$= \frac{nB'_1}{\beta_c - \beta_h} \cdot \left[\lim_{g\to 0} I(\alpha^*)\right]^{-1} \tag{7.7.72}$$

$$= \frac{nB'_1}{\beta_c - \beta_h} \cdot \left[\lim_{g\to 0} G(\alpha^*)\right]^{-1} \tag{7.7.73}$$

$$= \frac{nB'_1}{\beta_c - \beta_h} \cdot \frac{\beta_h}{n\alpha^{*2} B'_{\alpha^*}}. \tag{7.7.74}$$

The second equality holds by noting that both ΔC and W^*_α vanish in the limit $g \to 0$, and therefore apply the L'Hospital rule. In the third equality, we used the first derivative of ΔC as calculated in Eq. (7.3.31) of Lemma 7.5. Subsequently, we use Lemma 7.20 to calculate the value of $I(\alpha^*)$ in the quasi-static limit. Therefore, substituting Eq. (7.7.74) into the expression for efficiency in Eq. (7.7.70), we have Item 3, i.e.

$$\eta^{-1} = 1 + \lim_{g\to 0^+} \frac{\Delta C}{W_{\text{ext}}} \tag{7.7.75}$$

$$= 1 + \frac{\beta_h}{\beta_c - \beta_h} \frac{1}{\alpha^{*2}} \frac{B'_1}{B'_{\alpha^*}}. \tag{7.7.76}$$

□

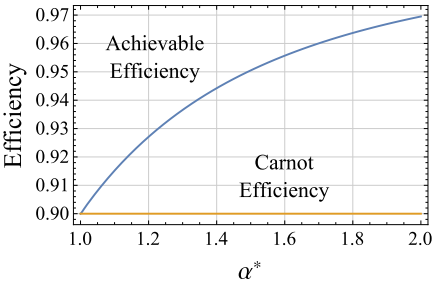

Figure 7.10: Achievable efficiency versus Carnot efficiency with respect to $\alpha^* \in (1,2)$, $\beta_h = 1$, $\beta_c = 10$ and $E = \frac{0.4}{\beta_c - \beta_h}$.

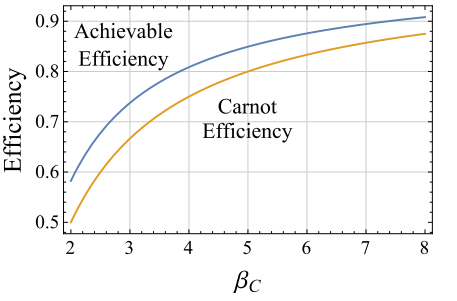

Figure 7.11: Achievable efficiency versus Carnot efficiency with respect to β_c, with $\alpha^* = 1.2$, $\beta_h = 1$, $E = \frac{0.4}{\beta_c - \beta_h}$.

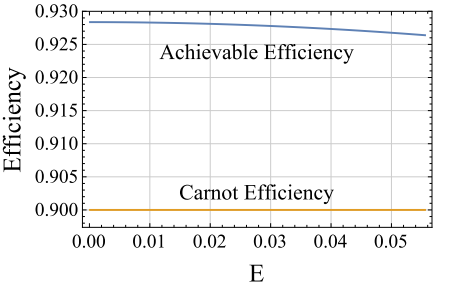

Figure 7.12: Achievable efficiency versus Carnot efficiency with respect to E, with $\alpha^* = 1.2$, $\beta_h = 1$, $\beta_c = 10$, $E = \frac{0.4}{\beta_c - \beta_h}$.

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With this, we can numerically plot out in Figures 7.10-7.12 the achievable efficiency as a function of $\beta_c, \beta_h, n, E, \alpha^*$, in the limit where $g \to 0^+$. It is worth noting that from Item 3) of Corollary 7.2, we see that the efficiency contains terms that originate from the expression of ε_1 chosen in Item 1) of the corollary. It is then, perhaps, unsurprising that we observe the surpassing of Carnot efficiency (for some values of $\alpha^* > 1$). Indeed, although the average energy change in the battery is positive, i.e. $\Delta W = (1-\varepsilon)W_{\text{ext}} > 0$, the change in *free energy* of the battery,

$$\Delta F_{\text{W}} = F(\rho_{\text{W}}^1) - F(\rho_{\text{W}}^0) = \Delta W - \beta_h^{-1}\Delta S, \tag{7.7.77}$$

is actually negative. This can be seen when we compute the limit

$$\lim_{g\to 0^+} \frac{\Delta F_{\text{W}}}{\Delta W} = \lim_{g\to 0^+} \frac{\Delta W - \beta_h^{-1}\Delta S}{\Delta W} = 1 - \beta_h^{-1} \lim_{g\to 0^+} \frac{\Delta S}{(1-\varepsilon)W_{\text{ext}}} = -\infty,$$

where the last limit comes from noting that $\lim_{g\to 0^+} \varepsilon = 0$, and applying Lemma 7.19. It is worth noting that Eq. (7.7.67) is in the regime where if one considers drawing near perfect work, it is always possible to achieve arbitrarily close to Carnot efficiency. Therefore, the blue curve never falls below the yellow line. The improvement in efficiency happens most when the parameter α^* is adjusted, since this is the parameter that determines how quickly the ratio $\frac{\Delta S}{W_{\text{ext}}} \to \infty$ in the quasi-static limit.

7.8. CONCLUSIONS AND OUTLOOK

In this chapter, we have applied the generalized second laws derived in Chapter 4 of the thesis to the setting of a quantum heat engine. We analyze the attainable efficiency for four qualitatively different regimes of work extraction.

In the first regime of perfect work, we show that a quantum heat engine can never extract perfect work by operating between two thermal baths. This can be seen by invoking the generalized second law for $F_0(\rho\|\tau)$, which is related to the relative rank of state ρ with respect to τ. Intuitvely, this can be understood as meaning that since thermal baths have a non-zero occupational probability (however small) across all energy levels, it becomes impossible to distill work with zero failure probability. However, we also show that work can be extracted once an arbitrarily small amount of failure probability $\varepsilon > 0$ is allowed.

In the subsequent sections, we analyze near perfect work, where not only the failure probability of work extraction $\varepsilon > 0$ is small, but also the amount of entropy created ΔS is negligible relative to the amount of work extracted W_{ext}. This corresponds to the regime where $\frac{\Delta S}{W_{\text{ext}}}$ is arbitrarily small. We show that the generalized second laws still allow for the achievability of Carnot efficiency, remarkably even for the case where one of the thermal baths is finite in size (even when the cold bath consists of just one qubit!). However, the achievability of Carnot efficiency does not longer hold for arbitrary bath Hamiltonians. This represents a fundamental diversion from classical thermodynamics.

An interesting observation during the course of our work, but omitted in this thesis, is the fact that the machine is a necessary component for achieving the Carnot efficiency while extracting near perfect work. In other words, the state transition $\rho^0_{\text{ColdW}} \to \rho^1_{\text{ColdW}}$ for the case of a quasi-static heat engine can only be achieved via *catalytic thermal operations*, instead of simply thermal operations. This emphasizes the importance of a physical object used to extract work while possibly undergoing a cyclic process, while successively interacting with both thermal baths. Therefore, when designing quantum heat engines, this should be taken into account, and whenever small errors occur, the issue of embezzling should always be discussed to ensure a fair evaluation of the heat engine's efficiency.

Finally, we investigated two regimes of imperfect work: 1) $\frac{\Delta S}{W_{\text{ext}}}$ is non-zero but finite, and 2) where $\frac{\Delta S}{W_{\text{ext}}} \to \infty$. For Case 1), Carnot efficiency remains an upper bound to the efficiency of quantum heat engines according to the generalized second laws. However, if one were to only invoke the macroscopic second law as a condition for state transition, then Carnot efficiency can be surpassed. For Case 2), we show examples where Carnot efficiency can be surpassed. This shows that our characterization of work has successfully captured the idea that heat contributions that pollute the extracted energy, if not properly accounted for, will lead to the illusion that one might exceed Carnot efficiency.

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CONCLUSIONS AND OUTLOOK

This is a concluding chapter, that provides a brief reflection and summary of all the scientific contributions presented in this thesis. An outlook for future research follows, where I outline the main steps one should take in seeking experimental verification of these theoretical predictions.

8.1. SUMMARY OF THESIS CONTRIBUTIONS

We summarize the findings that have contributed to our understanding of the foundations of quantum thermodynamics:

- *Derivation of generalized second laws*
  - ⋆ We started out from the framework of thermal operations, and extended it by allowing the inclusion of a *catalyst*, which is any additional, finite-size quantum system that is returned to its exact initial state at the end of the process. With this, we derive a family of generalized free energies $F_\alpha(\rho, \hat{H})$ where $\alpha \in \mathbb{R}$, defined in Eq. (4.5.64), page 62 for states block-diagonal in the energy eigenbasis. We have shown that for a system S with Hamiltonian $\hat{H}_S$, the possibility of a state transition $\rho_S \to \rho'_S$ via catalytic thermal operations, is dictated by whether for all $\alpha \in \mathbb{R}$, if we have that $F_\alpha(\rho_S, \hat{H}_S) \geq F_\alpha(\rho'_S, \hat{H}_S)$. These form necessary and sufficient conditions for transitions involving block-diagonal initial and final states.
  - ⋆ We also shown that the set of generalized laws for the case where $\alpha < 0$ can be eliminated, whenever one allows the usage of an additional ancilla such that it is returned $\varepsilon-$close to its original state (in particular, it is sufficient for such an ancilla to be 2-dimensional). This is desirable because the generalized free energies for $\alpha < 0$ are quantities which are unstable under perturbations of the rank of the quantum state.
  - ⋆ For abitrary, non-diagonal states, we show that the generalized second laws also hold, however they constitute necessary but insufficient conditions for a transition.
- *Unearthing and solving the problem of thermal embezzling*
  - ⋆ We consider a relaxed requirement on the catalyst, i.e. the catalyst is returned $\varepsilon-$close to its original state. We find that the form of the generalized second laws depend largely on the different measures used to quantify ε. We derive the consequences of inexact catalysis on the generalized second laws by using three different measures: 1) trace distance, 2) trace distance scaled by log of the catalyst dimension, and 3) the work distance. The problem of thermal embezzling occurs when only a requirement on trace distance is placed on the catalyst: all state transition conditions are nullified.
  - ⋆ Focusing on the case of a fully-degenerate (trivial) Hamiltonian, we find a special class of optimal catalyst initial and final pairs ω_C, ω'_C such that the trace distance $d(\omega_C, \omega'_C)$ is minimized, while going from ω_C to ω'_C allows the preparation of any state on a system S (therefore nullifying all generalized second laws).
  - ⋆ We identify physical restrctions such that thermal embezzling does not happen. We show that whenever the dimension of the catalyst is upper bounded, thermal embezzling does not happen. However, even when the catalyst is infinite-dimensional, as long as 1) the partition function Z_C is finite, and 2) the initial state ω_C has an upper bounded amount of average energy, thermal embezzling is also not possible anymore.
- *Application of the generalized second laws to the study of heat engines*
  - ⋆ We consider how the generalized second laws may be applied to a generic heat engine, that operates by interacting with two thermal baths of different temperature. We then

provide a way of characterizing the quality of work that divides extracted energy into three regimes: perfect, near perfect, and imperfect work. We show that for perfect and near perfect work extraction, heat engines that obey the macroscopic second law will be able to attain the Carnot efficiency, regardless of the bath Hamiltonian structure. This recovers in full rigour the results of Sadi Carnot in our heat engine model.

⋆ We evaluate the maximum efficiency for quantum heat engines obeying the generalized second laws, while considering again these three types of work. We find that the extraction of perfect work (with zero entropic contributions) becomes impossible. On the other hand, when considering near perfect work, Carnot efficiency remains a theoretical maximum for heat engines, however it is not anymore achievable regardless of the involved bath Hamiltonians. For the case of a cold bath consisting n qubits, we derive necessary and sufficient conditions on the bath Hamiltonian for the achievability of Carnot efficiency. Lastly, we show that if one considers the extraction of imperfect work, then Carnot efficiency can even be surpassed. This stresses the importance of using an appropriate definition of work in the quantum nanoregime, an issue which has usually not been sufficiently addressed for explicit quantum heat engine protocols.

8.2. AN OUTLOOK FOR FUTURE RESEARCH: EXPERIMENTAL VERIFICATION OF THEORETICAL PREDICTIONS

Quantum thermodynamics is still a new-rising, exciting field of research, with many open problems left to explore. In this concluding section, we will focus on expounding a particular theme for future research, which we believe to be of immediate succession of the contents in this thesis.

So far, findings in this area of research involve deriving fundamental limits to whether a state transition is possible. Such findings make predictions that are absent in classical macroscopic systems, and arise because the systems of interest are finite in size, and quantum-mechanical. The constructed framework is fully general in its applicability to quantum systems, and yet it captures the gist of how such systems may interact with a thermal environment. However, the key question still remains: Can these limits be reliably achieved in the real world? The experimental observations would determine, on a practical level, whether these theoretical predictions are truly relevant when it comes to assessing the performance of quantum-mechanical thermodynamic protocols. Should this be achieved, it would serve as a first step towards designing energy efficient nanoscale devices that can perform tasks such as work extraction and cooling [168].

Besides such practical significance, another important goal one hopes to achieve in the process of experimental implementation is a critical assessment of the current theoretical framework. Given its highly mathematical and abstract structure, the question arises whether TRTs can sufficiently describe the variety of experimental systems we have in the laboratory. This is likely to be true, since classical thermodynamics is also widely applicable, despite its simple premises. However, further development based on the current framework of TRTs (for example, adaptations which are more setup-specific) will be important in order to put the theory to the test. As discussed in Ref. [178] it remains a challenge to connect these powerful theoretical results with the relevant experimental systems. Therefore, working towards an experimental demonstration of TRTs also implies a great improvement

on the theoretical aspect, providing a coherent understanding of quantum thermodynamics.

There are three main steps towards this goal.

(A) SYSTEMATIC GENERALIZATION OF TRTS

The following comprises a selection of important generalizations one may perform, for a more complete description of TRTs, bringing them closer to testable predictions:

- *Proper energy accounting under more complex circumstances*
  Allowing more general forms of interaction Hamiltonian between system and bath, by accounting for non-energy preserving interactions justly. Currently, to ensure that energy is preserved during the thermodynamic process, the allowed interaction Hamiltonians are restricted to commute with the joint free Hamiltonian $\hat{H}_S + \hat{H}_B$ of the system (S) and bath (B). This however makes a non-trivial limitation on the number of possible ways to have coupling between systems. For a complete picture, it remains to perform a just energy accounting when more general coupling terms are allowed.

- *Generalizations regarding the usage of thermal baths*

  1. The state transition conditions could be generalized to the case where only a simple selection of thermal baths are available. This is due to the fact that although all Gibbs states (given any Hamiltonian) are justifiable resources, not all Gibbs states can be easily created, because not all quantum systems thermalize naturally. It would therefore be interesting to show whether all thermodynamic state transitions can still be achieved when only a set of naturally producable Gibbs states are accessible.
  2. By using various reservoir engineering techniques, it is possible to generate non-thermal/squeezed quantum reservoirs. From a resource-theory perspective, if one would allow the free usage of these reservoirs, then an arbitrary amount of work may be extracted. Such non-classical baths have been suggested to allow for efficiencies beyond the Carnot efficiency in context of trapped ions [160], however these notions are yet to be brought into contact with TRTs. Therefore, one may consider what is a meaningful way of quantifying work extraction rates, at the expense of using such additional, non-thermal resources.

- *Extension to infinite-dimensional/continuous variable systems*
  TRTs are currently formalized only for systems which can have arbitrarily large but finite dimensions. However, a large selection of quantum systems are continuous variable in nature, such as a quantized electromagnetic field, mechanical modes of opto-mechanical systems, and so on. One could therefore, adapt existing mathematical tools that govern information processing tasks for infinite-dimensional systems [179], and construct the corresponding generalization for TRTs.

(B) FINDING SUITABLE EXPERIMENTAL PLATFORMS

One has to identify relevant platforms of which the theory gives a natural description, in order to test the predictions of TRTs. In order to perform TRTs, one should choose an experimental setup where one can perform to a good approximation the following:

- initialize Gibbs states (to be used as thermal baths),

- initialize system of interest,
- switch on and off interaction Hamiltonians between system and bath quickly to implement the desired unitary operation,
- perform readouts with high fidelity.

Potential candidates commonly used for quantum computing include for example trapped ions, superconducting qubits, quantum dots, or cold atoms. TRT in its fully general form could also be tailored in more specific ways to better describe such specific systems. For example, consider the architectures of trapped ions, a setting in which recently a single ion heat engine has been realized [22]. In this context, ions confined in linear Paul traps with tapered geometry and can readily be driven thermally by coupling it alternately to hot and cold reservoirs, realized by exposing the ion to a laser cooling beam. This makes ions very natural candidates to facilitate interactions between different thermal reservoirs, as ancillary systems/catalysts. Thermal operations and their ramifications can also be explored in systems of cold atoms on top of atom chips, in which potentials to which the cold atoms are being subjected can be made programmable.

(C) DEVELOPMENT OF TOOLS TO CONCLUDE THE VERIFICATION OF THEORETICAL PREDICTIONS FROM EXPERIMENTAL DATA

The third question is immediate: what predictions can (or cannot) precisely be proven or verified experimentally? The list below comprises of possible implementation examples:

- Initialize a Gibbs state τ, an initial quantum state ρ and perform a specific set of thermal operations on the joint system, yielding final states $\{\sigma_i\}_i$. Perform quantum state tomography to identify the form of these states. Which generalized free energies can we conclude to have decreased in the process, given only a finite number of trials?
- Identify a work extraction protocol, resulting in the storage of energy in an ancillary system W. Assess the amount of energy fluctuations present in W. It would be interesting to devise a quantum heat engine that aims for near-perfect work and achieves the Carnot efficiency, which I have shown to be theoretically possible in Ref. [168].
- Demonstrate a protocol that uses a catalyst and returns it approximately, and show that one can embezzle work from such a process [125, 180].

Much of the above will require the development of appropriate certification tools that allow to assess whether the anticipated operation has actually been realised. This will be challenging, given that we aim for statements about the single-shot behaviour, given perhaps only a finite number of trials. For example, for any finite number of trials, measurement estimates from state tomography necessarily fluctuates around those of the true quantum state. A challenge is to distill confidence regions [181] where the true quantum state lies in with high probability, and evaluate the behaviour of generalized free energies in such confidence regions.

A thorough list of approaches and methods have been discussed in the three steps above, however one can see that each of these steps can be analyzed as subproblems, quite independently from each other.

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Appreciation is a wonderful thing.
It makes what is excellent in others belong to us as well.
Voltaire

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