Finite size effects in quantum thermodynamics

Ph.D. Thesis

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To everyone, who inspire me to do physics.

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Streszczenie

Termodynamika dostarcza fenomenologicznego opisu właściwości makroskopowych systemów w równowadze termicznej. Jest to jedna z fundamentalnych teorii służących do zrozumienia świata fizycznego, która została sformułowana bez podejmowania jakichkolwiek założeń dotyczących podstawowej struktury materii. Opisuje bardzo złożone, makroskopowe systemy o wielu stopniach swobody za pomocą kilku zmiennych termodynamicznych, takich jak objętość, temperatura, ciśnienie itp., których wartości zmieniają się bardzo powoli w atomowej skali czasu i są skrajnie gruboziarniste w atomowej skali odległości.

Termodynamika równowagowa zajmuje się makroskopowymi systemami, które składają się z nieskończonej liczby cząstek. W rezultacie prawa makroskopowej termodynamiki nie mogą być bezpośrednio stosowane w mikroskopowym zakresie, ponieważ rozmiar systemu jest skończony, co skutkuje możliwością pozostania poza stanem równowagi. Zachowanie systemu nie może być określone przez średnie zmiennych termodynamicznych, ponieważ fluktuacje tych zmiennych odgrywają kluczową rolę. Według klasycznej termodynamiki całkowita ilość pracy, która może zostać wydobyta z systemu, jest określana przez jego zmianę energii swobodnej, ale jest to prawdziwe tylko w przypadku, gdy mamy do czynienia z nieskończoną liczbą cząstek. W przypadku mniejszej liczby cząstek ilość pracy, którą można wydobyć, jest znacznie mniejsza niż zmiana energii swobodnej. Ta dyssypacja pracy wynika z wpływu fluktuacji na energię swobodną w reżimie skończonej wielkości.

Związek między fluktuacją zmiennej termodynamicznej a jej dyssypacją jest fundamentalnym pojęciem w nierównowagowej fizyce statystycznej, znanym jako związek fluktuacja-dyssypacja. W niniejszej pracy przedstawiamy wersję tego związku w ramach teorii zasobów, która bada optymalne przekształcenia stanów kwantowych poddanych ograniczeniom wynikającym z praw termodynamiki. Po pierwsze, charakteryzujemy optymalne procesy destylacji termodynamicznej i ustalamy związek między swobodną energią dyssypowaną w takich procesach a fluktuacjami energii swobodnej początkowego stanu systemu. Otrzymane przez nas związki fluktuacja-dyssypacja pozwalają na określenie optymalnej wydajności protokołów termodynamicznych, takich jak ekstrakcja pracy, wymazywanie informacji i termodynamicznie dozwolona komunikacja, z dokładnością do asymptot drugiego rzędu w liczbie przetwarzanych systemów.

Ponadto, niniejsza praca analizuje wpływ efektów skończonych rozmiarów na wydajność mikroskopowego silnika cieplnego. Tradycyjnie, dziedzina termodynamiki była rozwijana w celu wyjaśnienia pracy maszyn cieplnych na poziomie makroskopowym, takich jak lodówki, pompy ciepła i silniki cieplne. Jednak podczas opisywania tych maszyn na poziomie mikroskopowym konieczne staje się uwzględnienie efektów skończonych rozmiarów w opisie pracy i ciepła. Efekty kwantowe takie jak koherencja i korelacja wynikające z efektów skończonych rozmiarów mają istotny wpływ na produkcję pracy i wydajność silnika. Uogólnienie pojęć pracy i ciepła na poziomie mikroskopowym jest trudne i pozostaje tematem dyskusji, ponieważ wymaga uwzględnienia efektów skończonych rozmiarów. Jedną z powszechnie stosowanych miar pracy w reżimie mikroskopowym jest ergotropia, która odnosi się do maksymalnej ilości energii, która może być wyekstrahowana z systemu za pomocą operacji unitarnej. Rozprawa ta analizuje działanie mikroskopowego silnika cieplnego i demonstruje, jak jego wydajność może być poprawiona poprzez wykorzystanie korelacji z dodatkowym systemem pomocniczym, pełniącym rolę katalizatora.

Abstract

Thermodynamics provides a phenomenological description of the properties of macroscopic systems in thermal equilibrium. This is one of the fundamental theories to understand the physical world which has been formulated without making any assumptions about the underlying structure of matter. It describes very complex, macroscopic systems with many degrees of freedom by few simplified thermodynamic variables like volume, temperature, pressure etc., whose values change very slowly on the atomic scale of time and are extremely coarse on the atomic scale of distance.

Equilibrium thermodynamics deals with macroscopic systems that consist of an infinitely large number of particles. As a result, the laws of macroscopic thermodynamics cannot be straightforwardly applied to the microscopic regime, as the system's size is finite and there is a possibility of it remaining outside of an equilibrium state. The behaviour of the system cannot be determined by the average of the thermodynamic variables as the fluctuations in these variables play a pivotal role. According to classical thermodynamics, the total amount of work that can be extracted from a system is determined by its change in free energy, but this is only true if we are dealing with infinitely many particles. In the case of a smaller number of particles, the amount of work that can be extracted is considerably less than the change in free energy. This dissipation of work arises due to the influence of fluctuations on free energy in the finite size regime.

The relationship between the fluctuation of a thermodynamic variable and its dissipation is a fundamental concept in non-equilibrium statistical physics known as the fluctuation-dissipation relation. In this thesis, we present a version of this relation within a resource-theoretic framework that explores optimal quantum state transformations subject to constraints that arise from the laws of thermodynamics. Firstly, we characterize optimal thermodynamic distillation processes and establish a relationship between the free energy dissipated in such processes and the free-energy fluctuations of the initial state of the system. The fluctuation-dissipation relations we derive enable us to determine the optimal performance of thermodynamic protocols, such as work extraction, information erasure, and thermodynamically free communication, up to second-order asymptotics in the number of processed systems.

In addition, this thesis analyses how finite-size effects impact the performance of a microscopic heat engine. Traditionally, the field of thermodynamics was developed to explain the behaviour of thermal machines on a macroscopic level, such as refrigerators, heat pumps, and heat engines. However, while describing these machines at a microscopic level, incorporating finite-size effects into the description of work and heat becomes necessary. Quantum effects such as coherence and correlation that arise due to finite size have a significant impact on the work production and efficiency of the engine. Generalizing the notion of work and heat into the microscopic regime is challenging and remains a topic of debate, as it requires the inclusion of these finite-size effects. One common and widely used method of describing work in the microscopic regime is through ergotropy, which refers to the maximum amount of energy that can be extracted from a system via a unitary operation. This thesis analyzes the operation of a microscopic heat engine and demonstrates how

its performance can be improved by exploitation of correlation with an additional auxiliary system, serving as a catalyst.

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Lists of acronyms

acroglo : A la fois dans les deux *Glossaire:* acroglo

Glossary

acroglo :	A la fois dans les deux. xv

List of papers

This dissertation is based on the following published works and ongoing project:

1. *Fluctuation-dissipation relations for thermodynamic distillation processes* Tanmoy Biswas, A. de Oliveira Junior, Michał Horodecki, and Kamil Korzekwa *Phys. Rev. E 105, 054127*.
2. *Extraction of ergotropy: free energy bound and application to open cycle engines* Tanmoy Biswas, Marcin Łobejko, Paweł Mazurek, Konrad Jałowiecki and Michał Horodecki *Quantum 6, 841 (2022)*.
3. *Beating Otto efficiency with an engine assisted by a catalyst* Marcin Łobejko, Tanmoy Biswas, Paweł Mazurek, and Michał Horodecki *arXiv 23xx.xxxxx*.
4. *Catalytic advantage in the performance of quantum heat engine* Tanmoy Biswas, Marcin Łobejko, Paweł Mazurek, and Michał Horodecki *arXiv 23xx.xxxxx*.
5. *Discrete vs continious heat engine* Marcin Łobejko, Tanmoy Biswas, Paweł Mazurek, and Michał Horodecki *arXiv 23xx.xxxxx*.

Other published articles and preprints under review:

1. *Operational relevance of resource theories of quantum measurements.* Michał Oszmaniec and Tanmoy Biswas *Quantum 3, 133 (2019).*
2. *Interferometric visibility and coherence.* Tanmoy Biswas, María García Díaz and Andreas Winter *Proc. R. Soc. A 473 (2017), 10.1098/rspa.2017.0170.*
3. *Perfect discrimination of quantum measurements using entangled systems.* Chandan Datta, Tanmoy Biswas, Debashis Saha and Remigiusz Augusiak. *New J. Phys. 23 043021 (2021)*
4. *Optimal allocation of quantum resources* Roberto Salazar, Tanmoy Biswas, Jakub Czartowski, Karol Życzkowski and Paweł Horodecki *Quantum 5, 407 (2021).*
5. *Coarse-graining of measurement and quantum-to-classical transition in the bipartite scenario* Madhav Krishnan V, Tanmoy Biswas and Sibasish Ghosh *arXiv:1703.00502*

Introduction

Thermodynamics is a fundamental pillar of our understanding of the physical world. Historically, it was developed to analyze the performance of machines like steam engines and refrigerators [1]. The first theoretical steps towards it's formulation were taken over two centuries ago [2, 3, 4, 5, 6, 7], and even today, we continue to apply this theory to study systems that can help us advance our current available theories. For instance, black holes are studied in the hope of developing a theory of quantum gravity [8, 9, 10] using principles of thermodynamics. Thermodynamics was originally formulated as a phenomenological theory that describes thermal equilibrium. It characterizes a macroscopic system in a state of equilibrium, possessing numerous degrees of freedom, with the aid of simplified coordinates such as temperature, pressure, volume, and the number of particles. The values of these coordinates change at an extremely slow rate on the atomic scale of time, and they are extremely coarse on the atomic scale of length. Furthermore, the manifold of the equilibrium states is equipped with continuous and differentiable thermodynamic potentials such as entropy. The central theme of second law thermodynamics is to provide a complete characterization of interconversion among these equilibrium states utilizing these thermodynamic potentials [11, 12].

Moving from the macroscopic to a scenario consisting of a relatively smaller number of particles, the systems are more likely to be in a non-equilibrium state. Consequently, the characterization of conditions for interconversion among these non-equilibrium states becomes more intricate. In fact, the complete characterization of such inter-conversions has been a long-standing problem in statistical physics. However, modern thermodynamics has recently made significant progress in understanding the thermodynamics of out-of-equilibrium and quantum systems by utilizing the concepts from information theory. There is a long history of research of such thermodynamic entropy-like quantities in information theory [13] and matrix analysis [14, 15, 16] where it has been shown that several information-theoretic quantities exhibit universal features that resemble the second law of thermodynamics. The mathematical tools originally developed for communications and cryptography have emerged as fundamental building blocks underlying quantum theory and thermodynamics [13, 17]. In a series of papers [18, 19, 20, 21, 22, 23, 24, 25, 26], it has been established that the entropy of thermodynamics is nothing other than entropy in information entropy, which describes the lack of knowledge of the classical probability vector.

Unlike macroscopic systems, when examining small-scale systems, the thermodynamic quantities are subject to randomness due to the intrinsic stochasticity of the dynamics caused by the thermal fluctuations of heat baths. This is why modern thermodynamics is connected with information theory which is based on probability distributions and their transformation.

There are two main approaches to study small-scale thermodynamics that complements each other. The first is *stochastic thermodynamics* which has been developed in the field of nonequilibrium statistical mechanics. In this approach, relevant thermodynamic quantities like heat, work, energies etc. are considered stochastic variables and their averages and fluctuations are taken into account to describe non-equilibrium dynamics that present in microscopic systems [27, 28, 29]. and has resulted in a modern understanding of the thermodynamics of information [30, 31](See also chapter *Quantum fluctuation theorems* of [32]). Another approach to describe small-scale thermodynamics is the *resource theory of thermodynamics*, that is emerged as a branch utilizing the concepts and tools of quantum information theory that has been developed more recently. This perspective emphasizes that the second law of thermodynamics quantifies the amount of *resources* such as work, needed to complete a thermodynamic task [33, 34, 35, 36]. In contrast to the approach considered in stochastic thermodynamics, thermodynamic quantities like work are considered deterministic quantities rather than stochastic one. Resource theory is based on an information-theoretic framework that quantifies *useful resources*. The resource theory of entanglement, one of the earliest resource theories in quantum information theory [37, 38, 39] that shares a similar mathematical structure to the resource theory of thermodynamics. To formulate a resource theory, we must identify free states and free operations that can be prepared and performed without cost. In this thesis, we shall describe resource theory in the thermodynamical framework in detail.

This thesis adopts the resource theoretic approach of thermodynamics to investigate the consequences of surpassing the thermodynamic limit. Specifically, the study focuses on finite-size systems, which consist of a limited number of particles. Fluctuations of thermodynamic quantities become significant when analyzing the behaviour and transformation of such systems, particularly in the context of distilling pure energy eigenstates under thermodynamic constraints. The thesis characterizes optimal thermodynamic distillation processes and establishes a relationship between the free energy dissipated in such processes and the free-energy fluctuations of the initial system state. These results apply to initial states composed of either asymptotically many identical pure systems or an arbitrary number of independent energy-incoherent systems and allow for both state transformation and Hamiltonian change. The derived fluctuation-dissipation relations facilitate the determination of optimal performance for thermodynamic protocols, including work extraction, information erasure, and thermodynamically free communication, up to second-order asymptotics in the number of processed systems.

On other hand, the analysis of thermodynamic machines such as engines, coolers, and heat pumps differs significantly in the microscopic limit. Beyond the thermodynamic limit, the fundamental concepts of work and heat become ambiguous and are still the subject of debate among researchers. Additionally, quantum effects such as coherence and correlations have a significant impact on the behaviour of microscopic heat engines. One popular approach to quantify work in the microscopic system is through the concept of ergotropy, which approaches free energy in the thermodynamic limit, aligning with the second law of thermodynamics. Ergotropy is based on the notion that, even when a system is not in equilibrium, it is possible to extract useful work from it by applying external fields to induce transitions between different energy levels [40]. This thesis also aims to investigate the performance of a microscopic heat engine, which operates by inducing ergotropy from a heat bath and then storing it as work in a battery. This analysis leads us to consider a more general question: what is the maximum amount of ergotropy that can be induced in a system via an interaction with a heat bath? This thesis seeks to provide an answer to this question. Additionally, we explore the potential enhancement of the heat engine's performance through the use of a catalyst. This thesis is structured as follows:

Chapter 1 provides an overview of the key tools from information theory that are required to formulate a resource-theoretic framework for thermodynamics. Two fundamental concepts are introduced in this chapter: the first is information-theoretic entropies and divergences that measure the degree of disorder in a probability distribution and quantify the distance between two probability distributions. The second concept is majorization (and more generally, relative majorization), which characterizes the transformations between probability vectors. For further reading we recommend [13, 14, 15, 16].

Chapter 2 establishes the basis for the resource theory of thermodynamics, which is fundamental to this thesis. It introduces the concept of thermal operations and their characterization, which is critical to understanding energy transformation. Drawing on the ideas presented in 1 regarding relative majorization, we introduce the concept of *thermomajorization* to describe the transformation of energy incoherent states via thermal operations. This, in turn, enables us to define deterministic work using thermomajorization and formulate the second law of thermodynamics as the upper limit for work extraction. For further reading we shall recommend readers [33, 34, 35, 36, 41, 42, 43]. Moreover, a recent book [44] covers rigorously the resource theoretic formulation of thermodynamics.

Next chapters 3, 4, and 5 concern the research that I have done during my PhD.

Chapter 3 is built upon the work presented in [45]. We focus on thermodynamic distillation within the resource theoretic framework developed in Chapter 2 and investigate quantum state transformations under thermal operations. Our approach involves characterizing optimal thermodynamic distillation processes and proving a relationship between the amount of free energy dissipated during such processes and the free-energy fluctuations of the initial state of the system. By deriving fluctuation-dissipation relations, we can determine the optimal performance of thermodynamic protocols such as work extraction, information erasure, and thermodynamically free communication, up to second-order asymptotics in the number of processed systems.

Chapter 4 is based on the paper [46], which investigates the amount of ergotropy that can be induced in a system as a result of its interaction with a thermal bath, with the goal of utilizing it as a work source for microscopic machines. We model this interaction between the system and heat bath via thermal operation. We establish a fundamental upper bound on the amount of ergotropy that can be extracted from the heat bath via thermal operation that is expressed in terms of the non-equilibrium free energy difference. This bound can be attained in the limit of an infinite-dimensional system Hamiltonian. Furthermore, to support our result, we conduct a numerical simulation of the ergotropy extraction process for finite-dimensional systems and approach the obtained bound with the increase of dimensions.

Chapter 5, is based on the work [46] and ongoing projects on microscopic heat engines that aims to investigate two types of heat engines. The first engine operates through subsequent energy-conserving strokes, where the design incorporates an external control implicitly that regulates the sequence of these strokes. This particular microscopic heat engine operates by inducing ergotropy to the working body of the engine through interactions with a thermal bath. This interaction with the heat bath is modelled by thermal operation. The induced ergotropy is then stored in a battery as work using an energy conserving unitary operation on the working body and the battery. The second engine involves all components evolving by a single energy-conserving stroke, and thus requires no external control to function. We demonstrate how the laws of thermodynamics manifest in the operation of these microscopic engines. In addition, we have shown how their performance can be enhanced through the use of a catalyst. Finally, we have provided a dynamical model that simulates the performance of a catalyst assisted self-contained heat engine.

Chapter 1

Mathematical preliminaries

1.1 Introduction

This chapter introduces the fundamental mathematical concepts that are crucial for understanding the resource theory of thermodynamics. The key mathematical tools that aid in comprehending classical states and their transformations in thermodynamics are entropy, divergence, and majorization. In classical thermodynamics and information theory, entropy measures the degree of disorder in a system [11, 12, 21, 22]. Specifically, entropy fully characterizes the transformation among equilibrium states when there is no heat reservoir. Furthermore, divergence functions are used to calculate the distance between classical probability distributions [47, 48, 49, 44].

As we move away from conventional equilibrium situations, the inter-conversion among states becomes more complex. To characterize the conversion among different classical states, the majorization relation is used. Majorization is a comparison tool that allows us to compare probability distributions based on their ordering. These concepts are essential for describing classical states and their transformations.

Our exploration begins with defining classical states and dynamics through the use of finite-dimensional probability vectors and stochastic matrices. This sets the stage for developing the idea of majorization and relative majorization, which are essential for characterizing thermodynamic state transitions. Majorization plays a prominent role in the resource theories of entanglement, coherence, asymmetry, and purity. Meanwhile, the more general concepts of thermo-majorization and relative majorization are foundational in the resource theory of thermodynamics. To further our understanding, we provide a detailed explanation of various entropy and divergence functions, such as Shannon Entropy, Kullback-Leibler (KL) divergence, and α-Renyi entropy and divergence. In later sections, we briefly touch on additional divergence functions and their properties.

Overall, this chapter lays down the necessary mathematical foundations that helps in comprehending the complex workings of the resource theoretic framework of thermodynamics.

1.2 Classical state and their transformations

To build the foundation, we will establish our terminologies and notations from classical probability theory. To begin with, we shall define the classical states.

Definition 1 (Classical states)**.** We define the classical state as a probability vector

$$\boldsymbol{p} := (p_1, \dots, p_d)^T \in \mathcal{P}_d \quad \text{such that} \quad \forall i \quad p_i \geq 0 \quad \sum_{i=1}^{d} p_i = 1, \tag{1.1}$$

where T denotes the transpose. We shall denote the set of all classical states as $\mathcal{P}(d)$.

Here we introduce the classical state as a d-dimensional column vector. In the literature, the classical state is also known as *probability vector* or *population vector*. In this thesis, we shall use these terminologies with the same meaning. Given N independent classical states $\{\boldsymbol{p}\}_{i=1}^{N}$ where $\boldsymbol{p} \in \mathcal{P}_{d_i}$ one can define the joint classical state as

$$\boldsymbol{p}^N := \bigotimes_{i=1}^{N} \boldsymbol{p}_i \in \mathcal{P}_{d_1 d_2 \dots d_N}. \tag{1.2}$$

In the special case of the joint classical state of N systems being N independent and identically distributed (i.i.d.), we represent the joint classical state as $\boldsymbol{p}^{\otimes N} \in \mathcal{P}_{d^N}$. The support of $\boldsymbol{p}$, denoted by supp($\boldsymbol{p}$), is defined as the set of indices $i : p_i > 0$. Additionally, we define the rank of $\boldsymbol{p}$ as the cardinality of the support of $\boldsymbol{p}$, i.e., rank($\boldsymbol{p}$) $= |$supp($\boldsymbol{p}$)$|$.

The transformation of classical states is characterized by the action of a stochastic matrix that maps one classical state to the other. For simplicity, we assume that the dimension of the initial and final state is equal to d.

Definition 2 (Stochastic matrix)**.** A $d \times d$ stochastic matrix T is defined as a matrix whose elements are $T_{ij} \geq 0$ for all i, j and satisfy $\sum_{i=1}^{d} T_{ij} = 1$. In other words, each column of a stochastic matrix generates a valid probability vector.

The stochastic matrix T maps a classical state $\boldsymbol{p}$ to $\tilde{\boldsymbol{p}}$ as follows:

$$\tilde{\boldsymbol{p}} = T\boldsymbol{p} \quad \text{such that} \quad \tilde{p}_i = \sum_{j=1}^{d} T_{ij} p_j. \tag{1.3}$$

If the elements of a stochastic matrix satisfy $\sum_{j=1}^{d} T_{ij} = 1$ for all i, then it is referred as *bistochastic* matrix. Bistochastic matrices are those stochastic matrices whose rows generate a valid probability vector as well. Any bistochastic matrix preserves the uniform classical state u where $u = \frac{1}{d}(1, \ldots, 1)$. In other words, bistochastic matrix is *unital*.

Next, we will introduce the concept of *closeness* between two classical states by introducing various distance measures on the set of classical states. Several distance measures have been proposed in the literature [14, 44, 47, 15] to quantify the closeness between two classical states. However, in this discussion, we will focus on two fundamental distance measures that are commonly used for classical states: *trace distance* and *infidelity distance* which are defined below:

Definition 3 (Trace Distance)**.** The trace distance between two classical states $\boldsymbol{p},\ \boldsymbol{q} \in \mathcal{P}_d$ is defined as

$$D_{\text{Tr}}(\boldsymbol{p}, \boldsymbol{q}) := \frac{1}{2}\|p - q\|_1 = \frac{1}{2}\sum_{i=1}^{d} |p_i - q_i|. \tag{1.4}$$

Definition 4 (Infidelity distance)**.** The infidelity distance between two classical states $\boldsymbol{p},\ \boldsymbol{q} \in \mathcal{P}_d$ as

$$D(\boldsymbol{p}, \boldsymbol{q}) = 1 - \Big(\sum_{i=1}^{d} \sqrt{p_i q_i}\Big). \tag{1.5}$$

Both of the distance measures are valid metrics in $\mathcal{P}_d$ as it is obvious to see the distance measures satisfy *symmetry* and *positivity*. Employing Hölder's inequality [14], it is straightforward to see that distance measures satisfy triangle inequality as well. Moreover, the trace distance and infidelity distance are non-increasing under the transformation induced by a stochastic matrix T i.e.,

$$D_{\text{Tr}}(\boldsymbol{p}, \boldsymbol{q}) \geq D_{\text{Tr}}(T\boldsymbol{p}, T\boldsymbol{q}) \quad ; \quad D(\boldsymbol{p}, \boldsymbol{q}) \geq D(T\boldsymbol{p}, T\boldsymbol{q}). \tag{1.6}$$

This is referred to as *monotonicity* of the distance measures.

1.3 Entropy and divergence of classical states

In this section, we shall elucidate the concept of entropy for classical states and how to measure the divergence between different classical states. Similar to the distance measures between the probability vector introduced in the previous section, divergence between two classical states also captures the notion of *closeness* between two classical states. But contrary to the distance measures, we shall observe that divergences don't satisfy the symmetry. We prove some properties of entropy employing the characteristics of KL divergence or more generalized families of divergences. We shall start this section by defining Shannon Entropy and the KL Divergence. Later on, we shall use these concepts for a more general notion of entropies and divergences called α-Rényi entropy and divergences.

1.3.1 Shannon Entropy and the KL Divergence

Definition 5 (Shannon Entropy)**.** For a classical state $\boldsymbol{p} \in \mathcal{P}_d$ we define the *Shannon entropy* as

$$H(\boldsymbol{p}) = -\sum_{i=1}^{d} p_i \log p_i. \tag{1.7}$$

We shall define $0 \log 0 := 0$.

Definition 6 (KL divergence or Relative Entropy)**.** For two classical states $\boldsymbol{p}\ ,\ \boldsymbol{q} \in \mathcal{P}_d$, we define KL divergence or relative entropy as

$$D(\boldsymbol{p}\|\boldsymbol{q}) = \sum_{i=1}^{d} p_i \Big(\log p_i - \log q_i\Big). \tag{1.8}$$

If $\mathrm{supp}(\boldsymbol{p}) \nsubseteq \mathrm{supp}(\boldsymbol{q})$ we define $D(\boldsymbol{p}\|\boldsymbol{q}) := \infty$. From the definition, we see relative entropy $D(\boldsymbol{p}\|\boldsymbol{q})$ is asymmetric. To avoid complexity, we assume always $\mathrm{supp}(\boldsymbol{p}) \subseteq \mathrm{supp}(\boldsymbol{q})$. In the following proposition, we shall prove that relative entropy is always non-negative.

Proposition 1 (Non-negativity of the relative entropy)**.** *$D(\boldsymbol{p}\|\boldsymbol{q}) \geq 0$, for any two classical states $\boldsymbol{p},\ \boldsymbol{q} \in \mathcal{P}(d)$.*

Proof. Employing the identity $\log\left(x^{-1}\right) \geq (1-x)$ we can easily prove the non-negativity of the relative entropy as $D(\boldsymbol{p}\|\boldsymbol{q}) = \sum_{i=1}^{d} p_i \log\left(\frac{p_i}{q_i}\right) \geq \sum_{i=1}^{d} p_i \Big(1 - \frac{q_i}{p_i}\Big) = 0$. $\square$

Moreover, one can relate the relative entropy with Shannon entropy via the following relation:

$$H(\boldsymbol{p}) = \log d - D(\boldsymbol{p}\|\boldsymbol{u}), \tag{1.9}$$

where $\boldsymbol{u}$ is uniform classical state i.e., $\boldsymbol{u} = \frac{1}{d}(1 \ldots 1)$. From the non-negativity of the divergence $D(\boldsymbol{p}\|\boldsymbol{u}) \geq 0$, we conclude $H(\boldsymbol{p}) \leq \log d$. Relative entropy, like the distance measures introduced in Eq. (1.4) and Eq. (1.5) satisfies the monotonicity that is proven in the following proposition. In literature this relation sometimes referred as *data processing inequality*

Proposition 2 (Data processing inequality)**.** *For two given classical state **p** and **q** and a stochastic matrix T we have*

$$D(\boldsymbol{p}\|\boldsymbol{q}) \geq D(T\boldsymbol{p}\|T\boldsymbol{q}). \tag{1.10}$$

Proof. Let us denote that $T\boldsymbol{p} = \tilde{\boldsymbol{p}}$ and $T\boldsymbol{q} = \tilde{\boldsymbol{q}}$. To prove the claim we proceed as follows:

$$\begin{aligned} D(\boldsymbol{p}\|\boldsymbol{q}) - D(\tilde{\boldsymbol{p}}\|\tilde{\boldsymbol{q}}) &= \sum_{i=1}^{d} p_i \log\left(\frac{p_i}{q_i}\right) - D(\tilde{\boldsymbol{p}}\|\tilde{\boldsymbol{q}}) \\ &= \sum_{ij} T_{ji}p_i \log\left(\frac{T_{ji}p_i}{T_{ji}q_i}\right) - \sum_{j=1}^{d} \tilde{p}_j \log\left(\frac{\tilde{p}_j}{\tilde{q}_j}\right) \\ &= \sum_{ij} \tilde{p}_j \frac{T_{ji}p_i}{\tilde{p}_j} \log\left(\frac{T_{ji}p_i/\tilde{p}_j}{T_{ji}q_i/\tilde{q}_j}\right) = \sum_{ij} \tilde{p}_j D(\bar{\boldsymbol{p}}^{(j)}\|\bar{\boldsymbol{q}}^{(j)}) \geq 0, \end{aligned} \tag{1.11}$$

where $\bar{p}_i^{(j)} = \frac{T_{ji}p_i}{\tilde{p}_j}$ and $\bar{q}_i^{(j)} = \frac{T_{ji}q_i}{\tilde{q}_j}$. Note that in the last line Eq. (1.11) we have used non-negativity of relative entropy. □

We would like to make two remarks here. First, the converse of the proposition 2 is not true. Thus, relative entropy is not a *complete monotone* in the terminology of quantum resource theory. Second, If T is a bistochastic matrix then its action on uniform classical state $\boldsymbol{u} = \frac{1}{d}(1, \ldots, 1)$ is invariant i.e., $T\boldsymbol{u} = \boldsymbol{u}$. Then

$$\begin{aligned} & D(\boldsymbol{p}\|\boldsymbol{u}) = \log d - H(\boldsymbol{p}) \geq D(T\boldsymbol{p}\|\boldsymbol{u}) = \log d - H(T\boldsymbol{p}) \\ \Rightarrow\ & H(T\boldsymbol{p}) \geq H(\boldsymbol{p}), \end{aligned} \tag{1.12}$$

that says Shannon entropy is non-decreasing under a bistochastic map. In particular, from the relation given in Eq. (1.12) we can infer that Shannon entropy is a concave function over the set of classical state. Later on, we shall see Shannon entropy is *Schur concave* (We shall introduce Schur concavity later in this chapter). We conclude this section by introducing another important information-theoretic quantity called *mutual information*.

Definition 7 (Mutual information)**.** Let $\boldsymbol{p}_{AB}$ be a joint distribution of combined system A and B, and $\boldsymbol{p}_A$ and $\boldsymbol{p}_B$ is the corresponding marginal distribution of system A and B. The mutual information is defined as

$$I(\boldsymbol{p}_{AB})_{A:B} := D(\boldsymbol{p}_{AB}\|\boldsymbol{p}_A \otimes \boldsymbol{p}_B) = H(\boldsymbol{p}_A) + H(\boldsymbol{p}_B) + H(\boldsymbol{p}_{AB}). \tag{1.13}$$

Clearly the quantity $I(A:B) \geq 0$. The equality holds if and only if the joint classical state of the system A and B is statistically independent i.e., $\boldsymbol{p}_{AB} = \boldsymbol{p}_A \otimes \boldsymbol{p}_B$. From data processing inequality we immediately see $I(\boldsymbol{p}_{AB})_{(A:B)} \geq I(T_A \otimes T_B \boldsymbol{p}_{AB})_{A:B}$. In the following sections, we shall discuss more general forms of entropies and divergences.

1.3.2 Rényi Entropy and divergence

In this section, we will be introducing the concept of generalized entropies and divergences, namely the Rényi α-entropies and divergences for values $0 \leq \alpha \leq \infty$. These measures are essential in both information theory and statistics, and they extend the concepts of Shannon entropy and Kullback-Leibler divergence to more generalized cases. The Rényi entropy, with a parameter α, quantifies the degree of uncertainty or randomness in a given probability distribution, while the Rényi divergence measures the dissimilarity between two probability distributions, similar to the KL divergences. This section will explore the several useful properties of the Rényi entropy and divergence, including the chain rule, data processing inequality, and convexity. To start off, we will provide definitions for the Rényi entropy and divergence.

Definition 8 (Rényi Entropy)**.** For a classical state $\boldsymbol{p} \in \mathcal{P}_d$, the Renyi α-entropy is defined as

$$H_\alpha(\boldsymbol{p}) := \frac{1}{1-\alpha} \log \Big(\sum_{i=1}^{d} p_i^\alpha \Big), \tag{1.14}$$

where $0 \le \alpha \le \infty$. Here, $H_\alpha(\boldsymbol{p})$ for $\alpha = 0, 1, \infty$ is defined by taking the limit. It is straightforward to see that

$$\begin{aligned} H_0(\boldsymbol{p}) &= \log(\text{rank}[\boldsymbol{p}]) &(1.15)\\ H_\infty(\boldsymbol{p}) &= -\log(\max_i\{p_i\}) &(1.16) \end{aligned}$$

We also denote the quatities by $H_{\text{min}}(\boldsymbol{p}) := H_\infty(\boldsymbol{p})$ and $H_{\text{max}}(\boldsymbol{p}) := H_0(\boldsymbol{p})$, which referred as *min* and *max* entropies, respectively. It is obvious that

$$H_\alpha(\boldsymbol{p}) \ge 0. \tag{1.17}$$

Next, we shall address the limit $\alpha \to 1$ where Renyi Entropy boils down to Shannon entropy.

Proposition 3. *In the limit $\alpha \to 1$ Renyi α- entropy converges to Shannon entropy i.e.,*

$$\lim_{\alpha \to 1} H_\alpha(\boldsymbol{p}) = H(\boldsymbol{p}). \tag{1.18}$$

Proof. Using L'Hospital's rule we shall calculate this limit $\lim_{\alpha\to 1} H_\alpha(\boldsymbol{p})$ as

$$\lim_{\alpha \to 1} \frac{1}{1-\alpha} \log \Big(\sum_{i=1}^{d} p_i^\alpha \Big) = \lim_{\alpha \to 1} -\Big(\frac{\sum_{i=1}^{d} p_i^\alpha \log p_i}{\sum_{i=1}^{d} p_i^\alpha} \Big) = -\sum_{i=1}^{d} p_i \log p_i = H(\boldsymbol{p}). \tag{1.19}$$

. □

We next consider the Renyi α- divergence for classical states $\boldsymbol{p}, \boldsymbol{q} \in \mathcal{P}_d$ with $0 \le \alpha \le \infty$.

Definition 9 (Renyi α- divergence)**.** For d- dimensional classical state $\boldsymbol{p}$ and $\boldsymbol{q}$, the Renyi α-

divergence is defined between $\boldsymbol{p}$ and $\boldsymbol{q}$ as

$$D_\alpha(\boldsymbol{p}\|\boldsymbol{q}) := \frac{1}{\alpha-1}\log\Big(\sum_{i=1}^{d}\frac{p_i^\alpha}{q_i^{\alpha-1}}\Big). \tag{1.20}$$

For $\alpha = 0, 1, \infty$, we formulate them by taking the limit. It is easy to see the following:

$$\begin{aligned} D_0(\boldsymbol{p}\|\boldsymbol{q}) &= -\log\Big(\sum_{i:p_i>0} q_i\Big), \\ D_\infty(\boldsymbol{p}\|\boldsymbol{q}) &= \log\Big(\max_i\Big\{\frac{p_i}{q_i}\Big\}\Big). \end{aligned} \tag{1.21}$$

Contrary to the entropy case, as before we shall refer $D_{\text{min}}(\boldsymbol{p}\|\boldsymbol{q}) = D_0(\boldsymbol{p}\|\boldsymbol{q})$ and $D_{\text{max}}(\boldsymbol{p}\|\boldsymbol{q}) = D_\infty(\boldsymbol{p}\|\boldsymbol{q})$. Now, we shall calculate the limiting case of $\alpha \to 1$. In this limit we shall show that $D_\alpha(\boldsymbol{p}\|\boldsymbol{q})$ converges to KL divergence.

Proposition 4. *In the limit $\alpha \to 1$ Renyi α- divergence converges to relative entropy i.e.,*

$$\lim_{\alpha\to 1} D_\alpha(\boldsymbol{p}\|\boldsymbol{q}) := D(\boldsymbol{p}\|\boldsymbol{q}). \tag{1.22}$$

Proof. We shall use the L'Hospital rule as in proposition 3 to calculate the limit $\alpha \to 1$

$$\lim_{\alpha\to 1} D_\alpha(\boldsymbol{p}\|\boldsymbol{q}) = \lim_{\alpha\to 1}\frac{1}{\alpha-1}\log\Big(\sum_{i=1}^{d}\frac{p_i^\alpha}{q_i^{\alpha-1}}\Big) = \lim_{\alpha\to 1}\frac{1}{\Big(\sum_{i=1}^{d}\frac{p_i^\alpha}{q_i^{\alpha-1}}\Big)}\frac{d}{d\alpha}\Big(\sum_{i=1}^{d}\frac{p_i^\alpha}{q_i^{\alpha-1}}\Big) \tag{1.23}$$

$$= \lim_{\alpha\to 1}\frac{1}{\Big(\sum_{i=1}^{d}\frac{p_i^\alpha}{q_i^{\alpha-1}}\Big)}\sum_{i=1}^{d}\Big(q_i^{1-\alpha}p_i^\alpha\log p_i - p_i^\alpha q_i^{1-\alpha}\log q_i\Big) = \sum_{i=1}^{d}(p_i\log p_i - p_i\log q_i) = D(\boldsymbol{p}\|\boldsymbol{q}).$$

□

To extend this further, one can introduce a more general classes divergences called f-divergence where f is a real valued convex function. This general classical divergences will allow us to prove some important properties of Renyi α divergences. We shall start with the formal definition of convexity and concavity.

Definition 10 (Convex and concave function)**.** A function $f : \mathbb{R} \to \mathbb{R}$ is convex if $\forall\lambda \in [0, 1]$,

$$f\big(\lambda x + (1-\lambda)y\big) \le \lambda f(x) + (1-\lambda)f(y), \tag{1.24}$$

and f is concave if

$$f\big(\lambda x + (1-\lambda)y\big) \ge \lambda f(x) + (1-\lambda)f(y). \tag{1.25}$$

Moreover, we shall say f is *strictly convex (concave)* if the inequalities are strict.

Now we shall define f- divergence as follows:

Definition 11 (f-divergence)**.** Let $f : \mathbb{R}_{\geq 0} \to \mathbb{R}$ be a convex function such that $f(x)$ is strictly convex at $x = 1$ and $f(1) = 0$. For two classical states $\boldsymbol{p},\ \boldsymbol{q} \in \mathcal{P}_d$, f divergence is defined as follows:

$$D_f(\boldsymbol{p}\|\boldsymbol{q}) = \sum_{i=1}^{d} q_i f\Big(\frac{p_i}{q_i}\Big). \tag{1.26}$$

Employing Jensen's inequality for convex function one can show the non-negativity of f-divergence i.e., $D_f(\boldsymbol{p}\|\boldsymbol{q}) \geq 0$ in the following way:

$$\sum_{i=1}^{d} q_i f\Big(\frac{p_i}{q_i}\Big) \geq f\Big(\sum_{i=1}^{d} q_i \frac{p_i}{q_i}\Big) = f(1) = 0. \tag{1.27}$$

The equality holds iff $\boldsymbol{p} = \boldsymbol{q}$. We shall now consider three special cases of convex function f that leads to the familiar KL divergence, trace and infidelity distances.

1. Taking $f(x) = x \log x$ reduces $D_f(\boldsymbol{p}\|\boldsymbol{q})$ to relative entropy $D(\boldsymbol{p}\|\boldsymbol{q})$.
2. Taking $f(x) = \frac{1}{2}|x-1|$ reduces $D_f(\boldsymbol{p}\|\boldsymbol{q})$ to trace distance $D_{\text{Tr}}(\boldsymbol{p}, \boldsymbol{q})$.
3. Taking $f(x) = 1 - \sqrt{x}$ reduces $D_f(\boldsymbol{p}\|\boldsymbol{q})$ to infidelity distance $D(\boldsymbol{p}, \boldsymbol{q})$.

Next we shall show that the Data processing inequality does hold for f-divergences.

Lemma 5. *Let f be a convex function and $\boldsymbol{p},\ \boldsymbol{q},\ \tilde{\boldsymbol{p}},\ \tilde{\boldsymbol{q}} \in \mathcal{P}_d$ are classical states where $\boldsymbol{q}$ and $\tilde{q}$ are full rank. If $\tilde{p} = T\boldsymbol{p}$ and $\tilde{q} = T\boldsymbol{q}$ hold for stochastic matrix T, then*

$$D_f(\boldsymbol{p}\|\boldsymbol{q}) \geq D_f(\tilde{\boldsymbol{p}}\|\tilde{\boldsymbol{q}}). \tag{1.28}$$

Proof. We proceed the proof by noting

$$\frac{\tilde{p}_j}{\tilde{q}_j} = \sum_{i=1}^{d} \frac{T_{ji} q_i}{\tilde{q}_j} \frac{p_i}{q_i} \quad ; \quad \sum_{i=1}^{d} \frac{T_{ji} q_i}{\tilde{q}_j} = 1. \tag{1.29}$$

From the convexity of f and employing Jensen's inequality

$$\begin{aligned} D_f(\tilde{\boldsymbol{p}}\|\tilde{\boldsymbol{q}}) &= \sum_{j=1}^{d} \tilde{q}_j f\Big(\frac{\tilde{p}_j}{\tilde{q}_j}\Big) = \sum_{j=1}^{d} \tilde{q}_j f\left(\frac{\sum_{i=1}^{d} T_{ji} p_i}{\tilde{q}_j}\right) \\ &\leq \sum_{j=1}^{d}\sum_{i=1}^{d} \tilde{q}_j \frac{T_{ji} q_i}{\tilde{q}_j} f\Big(\frac{\tilde{p}_j}{\tilde{q}_j}\Big) = \sum_{i=1}^{d} q_i f\Big(\frac{p_i}{q_i}\Big) = D_f(\boldsymbol{p}\|\boldsymbol{q}). \end{aligned} \tag{1.30}$$

□

Next we shall prove some important properties of α-Renyi divergences employing the properties of f-divergences. We shall prove

1. Non-negativity.
2. Data processing inequality.
3. Monotonicity under the parameter α.

Proposition 6 (Non-negativity of the Renyi α divergence)**.** *For* $0 < \alpha \leq \infty$,

$$D_\alpha(\boldsymbol{p}\|\boldsymbol{q}) \geq 0. \tag{1.31}$$

Proof. Consider $f_\alpha(x) = x^\alpha - 1$, then $f_\alpha(x)$ is convex for $1 < \alpha < \infty$. Then

$$D_f(\boldsymbol{p}\|\boldsymbol{q}) = \sum_{i=1}^{d} q_i f\left(\frac{p_i}{q_i}\right) = \sum_{i=1}^{d} q_i \left(\frac{p_i}{q_i}\right)^\alpha - 1 = \sum_{i=1}^{d} \frac{p_i^\alpha}{q_i^{\alpha-1}} - 1 \geq 0, \tag{1.32}$$

where the last inequality follows from $D_f(\boldsymbol{p}\|\boldsymbol{q}) \geq 0$. This implies that

$$\begin{aligned} &\sum_{i=1}^{d} \frac{p_i^\alpha}{q_i^{\alpha-1}} \geq 1 \quad \Rightarrow \log\left(\frac{p_i^\alpha}{q_i^{\alpha-1}}\right) \geq 0 \quad \Rightarrow \frac{1}{\alpha-1} \log\left(\frac{p_i^\alpha}{q_i^{\alpha-1}}\right) \geq 0 \\ \Rightarrow \quad & D_\alpha(\boldsymbol{p}\|\boldsymbol{q}) \geq 0. \end{aligned} \tag{1.33}$$

For $0 < \alpha < 1$, f_α is concave, and thus we have the opposite inequality to the above. □

Proposition 7 (Data processing inequality for Renyi α-divergence)**.** *For any stochastic matrix* T*, the Renyi* α*-divergence with* $0 \leq \alpha \leq \infty$ *satisfies*

$$D_\alpha(\boldsymbol{p}\|\boldsymbol{q}) \geq D_\alpha(T\boldsymbol{p}\|T\boldsymbol{q}). \tag{1.34}$$

Proof. For $0 < \alpha < 1$ and $1 < \alpha < \infty$, we apply lemma 5 with $f_\alpha(x) = x^\alpha$ and take the logarithm of it, by noting the sign of $\alpha - 1$. For $\alpha = 0,\ 1,\ \infty$, we can take the limit. □

It is worth mentioning the connection α entropy and α divergence. Employing the uniform distribution $\boldsymbol{u}$, the α-divergence and α- entropy related as

$$H_\alpha(\boldsymbol{p}) = \log d - D_\alpha(\boldsymbol{p}\|\boldsymbol{u}), \tag{1.35}$$

from which we obtain $H_\alpha(\boldsymbol{p}) \leq \log d$. From the monotonicity of α- divergence, we have for any bistochastic matrix T we can get the monotonicity of α -entropy

$$H_\alpha(\boldsymbol{p}) \geq H_\alpha(T\boldsymbol{p}). \tag{1.36}$$

Next we shall show that Renyi α- divergence increases with the parameter α.

Proposition 8 (Monotonicity under parameter α)**.** *For $\alpha \leq \alpha'$, we have*

$$D_\alpha(\boldsymbol{p}\|\boldsymbol{q}) \leq D_{\alpha'}(\boldsymbol{p}\|\boldsymbol{q}), \tag{1.37}$$

and thus

$$\text{For } \alpha \leq \alpha', \qquad H_\alpha(\boldsymbol{p}) \geq H_{\alpha'}(\boldsymbol{p}). \tag{1.38}$$

Proof. For $\alpha < \alpha'$ taking $f(x) = x^{\frac{(\alpha-1)}{(\alpha'-1)}}$, we see that $f(x)$ is concave when $1 < \alpha < \alpha' < \infty$, while it is convex for $0 < \alpha < \alpha' < 1$ and $0 < \alpha < 1 < \alpha'$. From the Jensen's inequality, and noting the sign of $\alpha - 1$, we obtain

$$\begin{aligned} D_\alpha(\boldsymbol{p}\|\boldsymbol{q}) &= \frac{1}{\alpha-1}\log\left(\sum_i p_i\left(\frac{p_i}{q_i}\right)^{\alpha-1}\right) \\ &= \frac{1}{\alpha-1}\log\left(\sum_i p_i\left(\frac{p_i}{q_i}\right)^{\frac{\alpha-1}{\alpha'-1}(\alpha'-1)}\right) \\ &\leq \frac{1}{\alpha'-1}\log\left(\sum_i p_i\left(\frac{p_i}{q_i}\right)^{\alpha'-1}\right) = D_{\alpha'}(\boldsymbol{p}\|\boldsymbol{q}). \end{aligned} \tag{1.39}$$

For $\alpha,\ \alpha' = 0,\ 1,\ \infty$ we take the limit. Invoking equality from Eq. (1.35), we immediately see

$$\text{For } \alpha \leq \alpha', \qquad H_\alpha(\boldsymbol{p}) \geq H_{\alpha'}(\boldsymbol{p}). \tag{1.40}$$

□

In the next section we shall describe the interconvertibility among different classical states using the idea of majorization. Majorization is a mathematical concept that describes the relationship between two sets of numbers. It is commonly used to compare probability distributions, analyze inequalities, and study the properties of quantum systems. The majorization theory allows us to make quantitative statements about the ordering of different classical states and provide the necessary and sufficient condition for transformation among different classical states that we shall see shortly.

1.4 Ordering the classical states: majorization and relative majorization

In this section, we will describe the fundamentals of majorization and relative majorization, and their practical applications in interconverting between different classical states. Much like how the entropy function characterizes the transition between different equilibrium states, majorization fully characterizes the transition between different non-equilibrium classical states, either in the absence of a heat bath or when there is a heat bath present at an infinite temperature. Meanwhile, relative majorization is used to completely characterize the interconversion among different non-equilibrium states in the presence of a heat bath. We will discuss this in greater detail in the upcoming chapter. For now, we will start by exploring the majorization of classical states.

1.4.1 Majorization of classical states

When a bistochastic matrix maps a classical state $\boldsymbol{p}$ to $\boldsymbol{q}$, the Shannon entropy between the two states satisfies the monotonicity condition, where $H(\boldsymbol{q}) \geq H(\boldsymbol{p})$. However, it is important to note that the converse does not hold true. The Shannon entropy alone cannot serve as a sufficient condition for the convertibility between non-equilibrium classical states using a bistochastic matrix. In resource theory, the Shannon entropy of classical states is classified as a monotone under bistochastic matrix, but it is not a *complete monotone*.

For a classical states $(p_1, \ldots, p_d) := \boldsymbol{p} \in \mathcal{P}_d$ we define *ordered classical state* by arranging the elements of $\boldsymbol{p}$ in decreasing order as $p_1^{\downarrow} \geq p_2^{\downarrow} \geq \ldots p_d^{\downarrow}$. Now we shall define the majorization among classical states.

Definition 12 (Majorization)**.** For two vectors $\boldsymbol{p}$ and $\boldsymbol{p}'$, we say that $\boldsymbol{p}$ majorizes $\boldsymbol{p}'$ and write $\boldsymbol{p} \succ \boldsymbol{p}'$, if

$$\sum_{i=1}^{k} p_i^{\downarrow} \geq \sum_{i=1}^{k} p_i^{'\downarrow}, \qquad \forall 1 \leq k \leq d. \tag{1.41}$$

where $\boldsymbol{p}^{\downarrow}$ and $\boldsymbol{p}'^{\downarrow}$ denote non-increasingly ordered permutations of $\boldsymbol{p}$ and $\boldsymbol{p}'$.

This definition implies $\boldsymbol{p}$ is more ordered than $\boldsymbol{p}'$. Any classical states $\boldsymbol{p} \in \mathcal{P}_d$ satisfies

$$\begin{aligned} &\boldsymbol{v} \succ \boldsymbol{p} \succ \boldsymbol{u} \qquad \text{where} \\ &\boldsymbol{v} = (1, \ldots, 0) \quad ; \quad \boldsymbol{u} = \frac{1}{d}(1, \ldots, 1). \end{aligned} \tag{1.42}$$

Thus we can say $\boldsymbol{v}$ is the most ordered classical states whereas $\boldsymbol{u}$ is the least ordered classical states. Next we shall introduce *Lorenz* curves that will enable us to visualize the idea of majorization.

Definition 13 (Lorenz curves)**.** Let $L(\boldsymbol{p})$ be the piecewise linear curve in $\mathbb{R}^2$ obtained by joining the points $(k, \sum_{i=1}^{k} p_i^{\downarrow})$ for $k = \{1, \ldots, d\}$. We say that $L(\boldsymbol{p}) \succ L(\boldsymbol{q})$ if and only if the curve $L(\boldsymbol{p})$ all lies not below $L(\boldsymbol{q})$ and the two curves end at the same height.

As an example, here we shall present the Lorenz curves for some classical states in $\mathcal{P}_3$.

Now we are in a stage to describe the transition among different classical states and it's correspondence with majorization. This is stated in the following theorem:

Theorem 9. *Let $\boldsymbol{p}$ and $\boldsymbol{q}$ be the d dimensional classical states. Then following statements are equivalent.*

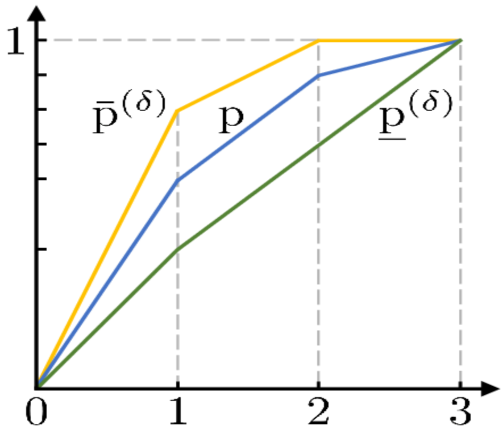


Figure 1.1: **Lorenz curve:** In this diagram we present the Lorenz curve of classical states $\bar{\boldsymbol{p}}^{\delta} = (0.8, 0.2, 0)$
(in orange), $\boldsymbol{p} = (0.6, 0.3, 0.1)$ (in blue), $\underline{\boldsymbol{p}}_{\delta} = (0.4, 0.3, 0.3)$ (in green). This diagram is taken from [50].

1. $\boldsymbol{p} \succ \boldsymbol{q}$.
2. For all $t \in \mathbb{R}$,
$$\sum_{i=1}^{d} |p_i - t| \geq \sum_{i=1}^{d} |q_i - t|. \tag{1.43}$$
3. For any convex function $f : \mathbb{R}_{\geq 0} \to \mathbb{R}$
$$\sum_{i=1}^{d} f(p_i) \geq \sum_{i=1}^{d} f(q_i). \tag{1.44}$$
4. There exists a bistochastic matrix T such that $T\boldsymbol{p} = \boldsymbol{q}$.

Proof. We shall prove the theorem in the following manner:

$$\text{Statement 4} \;\Rightarrow\; \text{Statement 3} \;\Rightarrow\; \text{Statement 2} \Leftrightarrow \text{Statement 1} \;\Rightarrow\; \text{Statement 4} \tag{1.45}$$

Statement 4 $\Rightarrow$ Statement 3
Given $\boldsymbol{q} = T\boldsymbol{p}$, we can have the following:

$$\sum_{i=1}^{d} f(q_i) = \sum_{i=1}^{d} f(\sum_{j=1}^{d} T_{ij} p_j) \leq \sum_{i=1}^{d} \sum_{j=1}^{d} T_{ij} f(p_j) = \sum_{j=1}^{d} \Big(\sum_{i=1}^{d} T_{ij} \Big) f(p_j) = \sum_{j=1}^{d} f(p_j), \tag{1.46}$$

where to write the last equality we use $\sum_{i=1}^{d} T_{ij} = 1$.

Statement 3 ⇒ Statement 2

For any $t \in \mathbb{R}$, the function $f(x) = |x - t|$ is convex function. One can simply check this as follows: For any $\lambda \in [0,1]$ and $x, y \in \mathbb{R}$

$$\begin{aligned} f(\lambda x + (1-\lambda)y) = |\lambda(x-t) + (1-\lambda)(y-t)| &\leq \lambda|x-t| + (1-\lambda)|y-t| \\ &= \lambda f(x) + (1-\lambda) f(y) \end{aligned} \tag{1.47}$$

Thus, taking the function $f(x) = |x - t|$, proves the claim.

Statement 2 ⇔ Statement 1

Suppose statement 1 holds true. Let $q^{\downarrow}_{k+1} \leq t \leq q^{\downarrow}_{k}$. Note that $\sum_{i=1}^{d} q_i = \sum_{i=1}^{d} p_i = 1$. This implies

$$\sum_{i=1}^{d} |q_i - t| = \sum_{i=1}^{k} (q^{\downarrow}_i - t) - \sum_{i=k+1}^{d} (q^{\downarrow}_i - t) \leq \sum_{i=1}^{k} (p^{\downarrow}_i - t) - \sum_{i=1}^{k+1} (p^{\downarrow}_i - t) \leq \sum_{i=1}^{d} |p_i - t|, \tag{1.48}$$

that implies statement 2.

Now assume that statement 2 holds true. Since, $\sum_{i=1}^{d} q_i = \sum_{i=1}^{d} p_i = 1$, taking $t = p^{\downarrow}_k$, then

$$\sum_{i=1}^{d} |p_i - t| = \sum_{i=1}^{k} (p^{\downarrow}_i - t) - \sum_{i=k+1}^{d} (p^{\downarrow}_i - t) = 2\sum_{i=1}^{k} p^{\downarrow}_i + (d-2k)t - 1. \tag{1.49}$$

On the other hand,

$$\sum_{i=1}^{d} |q_i - t| \geq \sum_{i=1}^{k} (q^{\downarrow}_i - t) - \sum_{i=k+1}^{d} (q^{\downarrow}_i - t) = 2\sum_{i=1}^{k} q_i + (d-2k)t - 1. \tag{1.50}$$

Thus statement 2 leads to the following conclusion:

$$\begin{aligned} & \sum_{i=1}^{d} |p_i - t| \geq \sum_{i=1}^{d} |q_i - t| \\ \Rightarrow \quad & 2\sum_{i=1}^{k} p_i + (d-2k)t - 1 \geq 2\sum_{i=1}^{k} q_i + (d-2k)t - 1 \\ \Rightarrow \quad & \sum_{i=1}^{k} p^{\downarrow}_i \geq \sum_{i=1}^{k} q^{\downarrow}_i \Rightarrow \boldsymbol{p} \succ \boldsymbol{q}, \end{aligned} \tag{1.51}$$

which is statement 1.

Statement 1 $\Rightarrow$ Statement 4

We shall prove the implication using the hyperplane separation theorem. Consider $\mathcal{B}$ is the set of $d \times d$ bistochastic matrices and define

$$\mathcal{B}(\boldsymbol{p}) = \{T\boldsymbol{p} \quad \text{such that } T \in \mathcal{B}\}. \tag{1.52}$$

Since the convex sum of any two bistochastic matrices is bistochastic, we can conclude that $\mathcal{B}(\boldsymbol{p})$ is a convex set. We shall do the proof by contradiction. Suppose $\boldsymbol{p} \succ \boldsymbol{q}$ but $\boldsymbol{q} \notin \mathcal{B}(\boldsymbol{p})$. That implies there exists a vector $\boldsymbol{r} \in \mathbb{R}(d)$ such that for all bistochastic matrix T, we have

$$(T\boldsymbol{p}, \boldsymbol{r}) < (\boldsymbol{q}, \boldsymbol{r}), \tag{1.53}$$

where $(\,\cdot\,,\,\cdot\,)$ denotes the standard inner product or dot product. Since the inequality in Eq. (1.53) does not change with the addition of a constant vector, thus we can assume all the components of $\boldsymbol{r}$ are non-negative. Let P and R are permutation matrices such that

$$\boldsymbol{p} = P\boldsymbol{p}^{\downarrow} \quad ; \quad \boldsymbol{r} = R\boldsymbol{r}^{\downarrow}. \tag{1.54}$$

Then we have the following:

$$(\boldsymbol{p}^{\downarrow}, \boldsymbol{r}^{\downarrow}) = (R^{\dagger}P^{\dagger}\boldsymbol{p}, \boldsymbol{r}) = (X\boldsymbol{p}, \boldsymbol{r}), \tag{1.55}$$

where $X = R^{\dagger}P^{\dagger}$ is a permutation matrix and thus T is bistochastic. Thus we can write

$$(\boldsymbol{p}^{\downarrow}, \boldsymbol{r}^{\downarrow}) = (X\boldsymbol{p}, \boldsymbol{r}) < (\boldsymbol{q}, r) = (R^{\dagger}\boldsymbol{q}, \boldsymbol{r}^{\downarrow}). \tag{1.56}$$

But in general if $\boldsymbol{x}, \boldsymbol{y} \in \mathbb{R}^d$ satisfy $\boldsymbol{x} \succ \boldsymbol{y}$, then for any $\boldsymbol{z} \in \mathbb{R}^d$ the following inequality holds:

$$(\boldsymbol{x}^{\downarrow}, \boldsymbol{w}^{\downarrow}) \geq (\boldsymbol{y}^{\downarrow}, \boldsymbol{w}^{\downarrow}). \tag{1.57}$$

From the statement 1, $\boldsymbol{p} \succ \boldsymbol{q}$ it follows that $\boldsymbol{p} \succ R^{\dagger}\boldsymbol{q}$ as $R^{\dagger}$ is a permutation matrix. Employing Eq. (1.57) we can write

$$(\boldsymbol{p}^{\downarrow}, \boldsymbol{r}^{\downarrow}) \geq ((R^{\dagger}\boldsymbol{q})^{\downarrow}, \boldsymbol{r}^{\downarrow}) \geq (R^{\dagger}\boldsymbol{q}, \boldsymbol{r}^{\downarrow}). \tag{1.58}$$

Therefore, inequality in Eq. (1.58) and Eq. (1.56) contradict with each other. Therefore, we can conclude that $\boldsymbol{q} \in \mathcal{B}(\boldsymbol{p})$. In other words, $\boldsymbol{q} = T\boldsymbol{p}$ where T is a bistochastic matrix. $\square$

We shall conclude this section by briefly describing Schur convex functions that are very useful to analyze the work extraction and performance of the heat engine. We shall see this in the upcoming chapter. We shall define Schur convexity as follows:

Definition 14 (Schur Convexity)**.** A function $F : \mathbb{R}^d \to \mathbb{R}$ is said to be Schur convex if

$$\boldsymbol{p} \succ \boldsymbol{q} \qquad \Rightarrow \quad F(\boldsymbol{p}) \geq F(\boldsymbol{q}). \tag{1.59}$$

On the other hand if $\boldsymbol{p} \succ \boldsymbol{q} \quad \Rightarrow \quad F(\boldsymbol{p}) \leq F(\boldsymbol{q})$, then F is called Schur concave. Shannon Entropy is a Schur concave function. This is easy to see as $\boldsymbol{p} \succ \boldsymbol{q}$ is equivalent to $T\boldsymbol{p} = \boldsymbol{q}$ where T is a bistochastic matrix. Entropy is non-decreasing when classical state is transformed under Bistochastic map which we have seen in Eq. (1.12). Now we shall introduce the relative majorization for classical states.

1.4.2 Relative majorization of classical states

The focus of this section is to discuss the concept of *relative majorization*, also known as *d-majorization*, which is a generalization of majorization for classical distributions. Relative majorization was originally introduced in the context of statistical comparison as a tool of examining convertibility between pairs of distributions. In contrast to ordinary majorization, which deals with convertibility from one distribution to another, relative majorization is concerned with convertibility between pairs of distributions. A specific type of relative majorization known as thermo-majorization characterizes a necessary and sufficient condition for state convertibility by thermodynamic processes at finite temperature $\beta > 0$.

To define relative majorization we need to introduce the concept of relative Lorenz curves. This is a generalization of Lorenz curves as introduced in definition 13.

Definition 15 (Relative Lorenz curves)**.** Consider a pair of probability vectors $\boldsymbol{p}$ and $\boldsymbol{q}$ given by

$$\boldsymbol{p} \;=\; (p_1, \ldots, p_d)^T \quad ; \quad \boldsymbol{q} = (q_1, \ldots, p_d)^T, \tag{1.60}$$

where $\boldsymbol{q}$ is full rank. We define the permutation π that arranges the components of $\boldsymbol{p}$ and $\boldsymbol{q}$ in the following way:

$$\frac{p_{\pi(1)}}{q_{\pi(1)}} \geq \frac{p_{\pi(2)}}{q_{\pi(2)}} \cdots \geq \frac{p_{\pi(d)}}{q_{\pi(d)}}. \tag{1.61}$$

Let $L_{\boldsymbol{q}}(\boldsymbol{p})$ be a piecewise linear curve in $\mathbb{R}^2$ obtained by joining $\left(\sum_{i=1}^k q_{\pi(i)}, \sum_{i=1}^k p_{\pi(i)}\right)$ for $k = 1, \ldots, n$. The curve $L_{\boldsymbol{q}}(\boldsymbol{p})$ is referred as relative Lorenz curve of the pair $(\boldsymbol{p}, \boldsymbol{q})$

Definition 16 (Relative majorization)**.** Consider two tuple of probaility vectors where $(\boldsymbol{p}, \boldsymbol{q})$ and $(\tilde{\boldsymbol{p}}, \tilde{\boldsymbol{q}})$ with $\boldsymbol{q}$ and $\tilde{\boldsymbol{q}}$ having full rank

$$\begin{aligned} \boldsymbol{p} &= (p_1, \ldots, p_d)^T \quad ; \quad \boldsymbol{q} = (q_1, \ldots, p_d)^T, \\ \tilde{\boldsymbol{p}} &= (\tilde{p}_1, \ldots, \tilde{p}_d)^T \quad ; \quad \tilde{\boldsymbol{q}} = (\tilde{q}_1, \ldots, \tilde{q}_d)^T. \end{aligned} \tag{1.62}$$

We say $(\boldsymbol{p}, \boldsymbol{q})$ *d-majorizes or relatively majorizes* $(\tilde{\boldsymbol{p}}, \tilde{\boldsymbol{q}})$ i.e., $(\boldsymbol{p}, \boldsymbol{q}) \succ (\tilde{\boldsymbol{p}}, \tilde{\boldsymbol{q}})$ if and only if the relative Lorenz curve $L_{\boldsymbol{q}}(\boldsymbol{p})$ does not lies below the relative Lorenz curve $L_{\tilde{\boldsymbol{q}}}(\tilde{\boldsymbol{p}})$.

Next, we shall describe the tool called *embedding* that connects the concepts of majorization and relative majorization.

1.4.2.1 Embedding: Relative majorization and majorization correspondance

In this section, we shall show the relation between majorization and relative majorization for classical states using the idea of the embedding map. We shall define the embedding map w.r.t a classical state $\boldsymbol{q}$ as follows:

Definition 17 (Embedding map)**.** Consider a given classical state $\boldsymbol{q}$ whose elements are approximated by rational numbers (Since any irrational number can be approximated with arbitrarily high accuracy with a rational number, this can be assumed without loss of generality)

$$\boldsymbol{q} = \Big(\frac{D_1}{D}, \ldots, \frac{D_d}{D}\Big), \quad D = \sum_{i=1}^{d} D_i. \tag{1.63}$$

Then an embedding map $\Gamma_{\boldsymbol{q}}$ w.r.t. classical state $\boldsymbol{q}$ maps a d-dimensional classical state $\boldsymbol{p}$ and to D-dimensional classical state $\hat{\boldsymbol{p}}$ as follows:

$$\begin{aligned} &\Gamma_{\boldsymbol{q}} : \ \mathcal{P}_d \longrightarrow \mathcal{P}_D \\ &\Gamma_{\boldsymbol{q}}(\boldsymbol{p}) = \Big(\underbrace{\frac{p_1}{D_1} \cdots \frac{p_1}{D_1}}_{D_1 \ \text{times}} \underbrace{\frac{p_2}{D_2} \cdots \frac{p_2}{D_2}}_{D_2 \ \text{times}} \cdots \underbrace{\frac{p_d}{D_d} \cdots \frac{p_d}{D_d}}_{D_d \ \text{times}} \Big) := \hat{\boldsymbol{p}}. \end{aligned} \tag{1.64}$$

It is straightforward to see the embedding map transforms $\boldsymbol{q}$ to $\hat{\boldsymbol{q}}$ as follows:

$$\hat{\boldsymbol{q}} = \Gamma_{\boldsymbol{q}}(\boldsymbol{q}) = \Big(\underbrace{\frac{1}{D} \cdots \frac{1}{D}}_{D_1 \ \text{times}} \underbrace{\frac{1}{D} \cdots \frac{1}{D}}_{D_2 \ \text{times}} \cdots \underbrace{\frac{1}{D} \cdots \frac{1}{D}}_{D_d \ \text{times}} \Big). \tag{1.65}$$

For a d-dimensional classical state $\boldsymbol{s}$ having j^{th} element 1 and all the element 0, the embedded version of the classical state

$$\hat{\boldsymbol{s}} = \Gamma_{\boldsymbol{q}}(\boldsymbol{s}) = \Big(\underbrace{0 \ldots 0}_{D_1 \ \text{times}} \ \underbrace{0 \ldots 0}_{D_2 \ \text{times}} \ \cdots \underbrace{\frac{1}{D_j} \cdots \frac{1}{D_j}}_{D_j \ \text{times}} \cdots \underbrace{0 \ldots 0}_{D_d \ \text{times}} \Big). \tag{1.66}$$

By writing down the matrix representing embedding map $\Gamma_{\boldsymbol{q}}$ explicitly, one can write the left inverse as follows:

$$\Gamma_{\boldsymbol{q}} = \begin{pmatrix} \frac{1}{D_1} & 0 & \dots & 0 \\ \vdots & \vdots & \dots & 0 \\ \frac{1}{D_1} & \vdots & \dots & 0 \\ 0 & \frac{1}{D_2} & \dots & 0 \\ \vdots & \vdots & \dots & 0 \\ 0 & \frac{1}{D_2} & \dots & 0 \\ \vdots & \vdots & \dots & \vdots \\ 0 & 0 & \dots & \frac{1}{D_d} \\ \vdots & \vdots & \dots & \vdots \\ 0 & \vdots & \dots & \frac{1}{D_d} \end{pmatrix}, \; \Gamma_{\boldsymbol{q}}^{-1} = \begin{pmatrix} 1 & \dots & 1 & 0 & \dots & 0 & \dots & \dots & \dots & 0 \\ 0 & \dots & 0 & 1 & \dots & 1 & \dots & \dots & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & \dots & 0 & 0 & \dots & 0 & \dots & 1 & \dots & 1 \end{pmatrix}. \tag{1.67}$$

where in each column i of $\Gamma_{\boldsymbol{q}}$ and each row i of $\Gamma_{\boldsymbol{q}}^{-1}$ there are D_i non-zero elements. The following theorem characterizes the transformation of pair of classical states via stochastic matrix in terms majorization of embedded classical states.

Theorem 10. *Consider two pairs of classical states* $(\boldsymbol{p}, \boldsymbol{q})$ *and* $(\tilde{\boldsymbol{p}}, \tilde{\boldsymbol{q}})$ *such that*

$$\tilde{\boldsymbol{p}} = T\boldsymbol{p} \quad ; \quad \tilde{\boldsymbol{q}} = T\boldsymbol{q}, \tag{1.68}$$

where T *is a stochastic matrix. Then* $\Gamma_{\boldsymbol{q}}\boldsymbol{p} \succ \Gamma_{\tilde{\boldsymbol{q}}}\tilde{\boldsymbol{p}}$.

Proof. We shall prove this theorem via constructing a bistochastic matrix B such that $B\Gamma_{\boldsymbol{q}}(\boldsymbol{p}) = \Gamma_{\tilde{\boldsymbol{q}}}(\tilde{\boldsymbol{p}})$. We define $B = \Gamma_{\tilde{\boldsymbol{q}}}T\Gamma_{\boldsymbol{q}}^{-1}$. It is straight forward to check that

$$B\Gamma_{\boldsymbol{q}}\boldsymbol{p} = \Gamma_{\tilde{\boldsymbol{q}}}T\Gamma_{\boldsymbol{q}}^{-1}\Gamma_{\boldsymbol{q}}\boldsymbol{p} = \Gamma_{\tilde{\boldsymbol{q}}}T\boldsymbol{p} = \Gamma_{\tilde{\boldsymbol{q}}}\tilde{\boldsymbol{p}}. \tag{1.69}$$

Next we shall show that B is bistochastic. To do show, we first show that B is stochastic. It is easy to check this by summing all the elements of a column in computational basis $|i\rangle$ i.e.,

$$\text{For fixed } j, \quad \sum_i \langle i|\Gamma_{\tilde{\boldsymbol{q}}}T\Gamma_{\boldsymbol{q}}^{-1}|j\rangle = 1. \tag{1.70}$$

Since any stochastic matrix preserves a uniform classical state is bistochastic, we shall show $B\boldsymbol{u} = \boldsymbol{u}$ where $\boldsymbol{u}$ is the uniform classical state.

$$B\boldsymbol{u} = \Gamma_{\tilde{\boldsymbol{q}}}T\Gamma_{\boldsymbol{q}}^{-1}\boldsymbol{u} = \Gamma_{\tilde{\boldsymbol{q}}}T\Gamma_{\boldsymbol{q}}^{-1}\Gamma_{\boldsymbol{q}}\boldsymbol{q} = \Gamma_{\tilde{\boldsymbol{q}}}T\boldsymbol{q} = \Gamma_{\tilde{\boldsymbol{q}}}\tilde{\boldsymbol{q}} = \boldsymbol{u}. \tag{1.71}$$

□

Now we shall establish the connection between relative majorization and majorization in the following theorem.

Theorem 11 (Blackwell's theorem)**.** *Let $\boldsymbol{p}, \boldsymbol{q}, \tilde{\boldsymbol{p}}, \tilde{\boldsymbol{q}}$ are d- dimensional probability vector where $\boldsymbol{q}$ and $\tilde{\boldsymbol{q}}$ have full rank. Then the following statements are equivalent.*

1. $(\boldsymbol{p}, \boldsymbol{q}) \succ (\tilde{\boldsymbol{p}}, \tilde{\boldsymbol{q}})$.
2. $\forall t \in \mathbb{R}$ *we have*
$$\sum_{i=1}^{d} |p_i - tq_i| \geq \sum_{i=1}^{d} |\tilde{p}_i - t\tilde{q}_i|. \tag{1.72}$$
3. *For every real-valued convex function $f : \mathbb{R} \to \mathbb{R}$ we have*
$$\sum_{i=1}^{d} q_i f\left(\frac{p_i}{q_i}\right) \geq \sum_{i=1}^{d} \tilde{q}_i f\left(\frac{\tilde{p}_i}{\tilde{q}_i}\right). \tag{1.73}$$
4. *There exists a stochastic matrix T such that $\tilde{\boldsymbol{p}} = T\boldsymbol{p}$ and $\tilde{\boldsymbol{q}} = T\boldsymbol{q}$.*

Proof. This theorem is analogous to theorem 9 in the majorization picture. We shall see that part of the proof of this theorem overlaps with the proof of theorem 9. We shall prove the theorem in the following manner:

$$\begin{aligned} &\text{Statement 4} \;\Rightarrow\; \text{Statement 3} \;\Rightarrow\; \text{Statement 2} \Leftrightarrow \text{Statement 1} \\ &\text{Statement 2} \Leftrightarrow \text{Statement 4} \end{aligned} \tag{1.74}$$

Statement 4 ⇒ Statement 3

It follows straightforwardly from lemma 5.

Statement 3 ⇒ Statement 2

It is easy to prove that by taking $f(x) = |x-t|$ for $t \in \mathbb{R}$. We showed that the $f(x) = |x-t|$ is convex in the proof of theorem 9.

Statement 2 ⇔ Statement 1

Let π and $\tilde{\pi}$ are the permutation that orders the component in the following way:

$$\begin{aligned} \frac{p_{\pi(1)}}{q_{\pi(1)}} \geq \frac{p_{\pi(2)}}{q_{\pi(2)}} \ldots \geq \frac{p_{\pi(d)}}{q_{\pi(d)}}, \\ \frac{\tilde{p}_{\tilde{\pi}(1)}}{\tilde{q}_{\tilde{\pi}(1)}} \geq \frac{\tilde{p}_{\tilde{\pi}(2)}}{\tilde{q}_{\tilde{\pi}(2)}} \ldots \geq \frac{\tilde{p}_{\tilde{\pi}(d)}}{\tilde{q}_{\tilde{\pi}(d)}}. \end{aligned} \tag{1.75}$$

Note that,

$$
\begin{aligned}
&[0, q_{\pi(1)}), [q_{\pi(1)}, q_{\pi(1)} + q_{\pi(2)}), \dots [q_{\pi(1)} + \dots + q_{\pi(d-1)}, 1], \\
&[0, \tilde{q}_{\tilde{\pi}(1)}), [\tilde{q}_{\tilde{\pi}(1)}, \tilde{q}_{\tilde{\pi}(1)} + \tilde{q}_{\tilde{\pi}(2)}), \dots [\tilde{q}_{\tilde{\pi}(1)} + \dots + \tilde{q}_{\tilde{\pi}(d-1)}, 1],
\end{aligned} \tag{1.76}
$$

are partition of the interval $[0,1]$. Take $\boldsymbol{q}' = (q'_1, \dots q'_{d'-1})$ such that

$$
[0, q'_1), [q'_1, q'_1 + q'_2), \dots [q'_1 + \dots + q'_{d'-1}, 1], \tag{1.77}
$$

gives refinement of both partition given in Eq. (1.76) of the interval $[0,1]$.

Now we shall take the probabiity vector $\boldsymbol{p}'$ and $\tilde{\boldsymbol{p}}'$ such that relative Lorenz curves for $(\boldsymbol{p}, \boldsymbol{q})$ is same with $(\boldsymbol{p}', \boldsymbol{q}')$ and relative Lorenz curves for $(\tilde{\boldsymbol{p}}, \tilde{\boldsymbol{q}})$ is same with $(\tilde{\boldsymbol{p}}', \tilde{\boldsymbol{q}}')$ i.e

$$
L_{\boldsymbol{q}}(\boldsymbol{p}) = L_{\boldsymbol{q}'}(\boldsymbol{p}') \quad ; \quad L_{\tilde{\boldsymbol{q}}}(\tilde{\boldsymbol{p}}) = L_{\boldsymbol{q}'}(\tilde{\boldsymbol{p}}'). \tag{1.78}
$$

Therefore, it is sufficient to show that statement 1 is equivalent to statement 2 for the pair $(\boldsymbol{p}', \boldsymbol{q}')$ and $(\tilde{\boldsymbol{p}}', \boldsymbol{q}')$ since $(\boldsymbol{p}, \boldsymbol{q}) \succ (\tilde{\boldsymbol{p}}, \tilde{\boldsymbol{q}}) \Leftrightarrow (\boldsymbol{p}', \boldsymbol{q}') \succ (\tilde{\boldsymbol{p}}', \boldsymbol{q}')$. We shall prove it in the same way as theorem 9.

Suppose statement 1 holds true i.e., $(\boldsymbol{p}', \boldsymbol{q}') \succ (\tilde{\boldsymbol{p}}', \boldsymbol{q}')$. Consider π' and $\tilde{\pi}'$ is the permutation that leads to following ordering:

$$
\begin{aligned}
&\frac{p'_{\pi'(1)}}{q'_{\pi'(1)}} \geq \frac{p'_{\pi'(2)}}{q'_{\pi'(2)}} \dots \geq \frac{p'_{\pi'(d')}}{q'_{\pi'(d')}}, \\
&\frac{\tilde{p}'_{\tilde{\pi}(1)}}{q'_{\tilde{\pi}'(1)}} \geq \frac{\tilde{p}'_{\tilde{\pi}(2)}}{q'_{\tilde{\pi}'(2)}} \dots \geq \frac{\tilde{p}'_{\tilde{\pi}(d')}}{q'_{\tilde{\pi}'(d')}}.
\end{aligned} \tag{1.79}
$$

Let $\frac{\tilde{p}_{\tilde{\pi}'(k+1)}}{q'_{\tilde{\pi}'(k+1)}} \leq t \leq \frac{\tilde{p}_{\tilde{\pi}'(k)}}{q'_{\pi'(k)}}$. Note that $\sum_{i=1}^{d} q_i = \sum_{i=1}^{d} p_i = 1$. This implies

$$
\begin{aligned}
\sum_{i=1}^{d} |\tilde{p}'_i - t q'_i| &= \sum_{i=1}^{d} q'_i \left| \frac{\tilde{p}'_i}{q'_i} - t \right| = \sum_{i=1}^{k} q'_{\tilde{\pi}'(i)} \Big(\frac{\tilde{p}_{\tilde{\pi}'(i)}}{q'_{\tilde{\pi}'(i)}} - t \Big) - \sum_{i=k+1}^{d} q'_{\tilde{\pi}'(i)} \Big(\frac{\tilde{p}_{\tilde{\pi}'(i)}}{q'_{\tilde{\pi}'(i)}} - t \Big) \\
\leq \ & \sum_{i=1}^{k} q'_{\pi'(i)} \Big(\frac{p'_{\pi'(i)}}{q'_{\pi'(i)}} - t \Big) - \sum_{i=k+1}^{d} q'_{\pi'(i)} \Big(\frac{p'_{\pi'(i)}}{q'_{\pi'(i)}} - t \Big) \\
\leq \ & \sum_{i=1}^{d} q'_i \left| \frac{p'_i}{q'_i} - t \right| = \sum_{i} |p'_i - t q'_i|,
\end{aligned} \tag{1.80}
$$

that implies statement 2. Other part of the proof can be done in the same manner of the theorem 9.

Statement 2 $\Rightarrow$ Statement 4

Now we shall prove the non-trivial part of this theorem. Let $\boldsymbol{q}$ and $\tilde{\boldsymbol{q}}$ as

$$\boldsymbol{q} = \frac{1}{D}(D_1\ D_2\ \dots\ D_d) \quad ; \quad \tilde{\boldsymbol{q}} = \frac{1}{D}(\tilde{D}_1\ \tilde{D}_2\ \dots\ \tilde{D}_d), \tag{1.81}$$

where $\sum_{i=1} D_i = \sum_{i=1} \tilde{D}_i = D$ which we can assume without loss of generality. Let $\Gamma_{\boldsymbol{q}}(p)$ and $\Gamma_{\tilde{\boldsymbol{q}}}(\tilde{\boldsymbol{p}})$ are embedded version of $\boldsymbol{p}$ and $\tilde{\boldsymbol{p}}$ respectively i.e.,

$$\begin{aligned}
\Gamma_{\boldsymbol{q}}(\boldsymbol{p}) &= \Big(\underbrace{\frac{p_1}{D_1}\dots\frac{p_1}{D_1}}_{D_1\ \text{times}}\ \underbrace{\frac{p_2}{D_2}\dots\frac{p_2}{D_2}}_{D_2\ \text{times}}\dots\underbrace{\frac{p_d}{D_d}\dots\frac{p_d}{D_d}}_{D_d\ \text{times}}\Big) := \hat{\boldsymbol{p}},\\
\Gamma_{\tilde{\boldsymbol{q}}}(\tilde{\boldsymbol{p}}) &= \Big(\underbrace{\frac{\tilde{p}_1}{\tilde{D}_1}\dots\frac{\tilde{p}_1}{\tilde{D}_1}}_{\tilde{D}_1\ \text{times}}\ \underbrace{\frac{\tilde{p}_2}{\tilde{D}_2}\dots\frac{\tilde{p}_2}{\tilde{D}_2}}_{\tilde{D}_2\ \text{times}}\dots\underbrace{\frac{\tilde{p}_d}{\tilde{D}_d}\dots\frac{\tilde{p}_d}{\tilde{D}_d}}_{\tilde{D}_d\ \text{times}}\Big) := \hat{\tilde{\boldsymbol{p}}}.
\end{aligned} \tag{1.82}$$

Taking from statement 2 of the theorem we can write $\forall t \in \mathbb{R}$

$$\sum_{i=1}^{D} \left|\hat{\tilde{p}}_i - \frac{t}{D}\right| \leq \sum_{i=1}^{D} \left|\hat{p}_i - \frac{t}{D}\right|. \tag{1.83}$$

Defining $t/M = \epsilon$ we have for all $\forall \epsilon \in \mathbb{R} \quad \sum_{i=1}^{D} |\hat{\tilde{p}}_i - \epsilon| \leq \sum_{i=1}^{D} |\hat{p}_i - \epsilon|$. From theorem 9 we conclude

$$\hat{\tilde{\boldsymbol{p}}} = \Gamma_{\boldsymbol{q}}\boldsymbol{p} \succ \Gamma_{\tilde{\boldsymbol{q}}}\boldsymbol{p} = \hat{\tilde{\boldsymbol{p}}}, \tag{1.84}$$

and thus

$$B\Gamma_{\boldsymbol{q}}\boldsymbol{p} = \Gamma_{\tilde{\boldsymbol{q}}}\boldsymbol{p}, \tag{1.85}$$

for a $D \times D$ bistochastic matrix B. Then it is easy to see from Eq. (1.82) and invoking unitality of bistochastic matrix, that the map

$$\Gamma_{\tilde{\boldsymbol{q}}}^{-1} B \Gamma_{\boldsymbol{q}} \boldsymbol{q} = \tilde{\boldsymbol{q}} \quad ; \quad \Gamma_{\tilde{\boldsymbol{q}}}^{-1} B \Gamma_{\boldsymbol{q}} \boldsymbol{p} = \tilde{\boldsymbol{p}}. \tag{1.86}$$

Moreover from the matrix representation of stochastic map given in Eq. (1.67) we can show that $\Gamma_{\tilde{\boldsymbol{q}}}^{-1} B \Gamma_{\boldsymbol{q}}$ is a stochastic matrix by showing all the entries in each of the column of matrix representation of $\Gamma_{\tilde{\boldsymbol{q}}}^{-1} B \Gamma_{\boldsymbol{q}}$ added to 1 as follows:

$$\text{For fixed } j, \quad \sum_i \langle i|\Gamma_{\tilde{\boldsymbol{q}}}^{-1} B \Gamma_{\boldsymbol{q}}|j\rangle = \langle u|B\Gamma_{\boldsymbol{q}}|j\rangle = \langle u|\Gamma_{\boldsymbol{q}}|j\rangle = 1, \tag{1.87}$$

where $|u\rangle$ is a uniform column vector with all the elements 1 and $\{|i\rangle\}_{i=1}^{d}$ is the computational basis in d dimension. ☐

Next, we shall provide the conditions for state transformations in terms of min and max divergences.

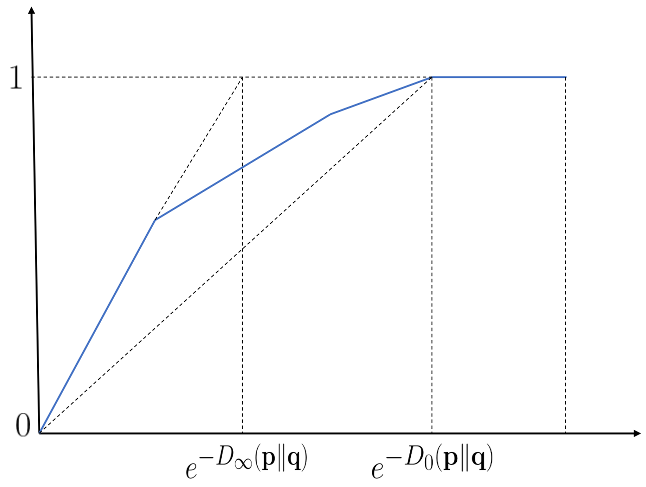


Figure 1.2: The Lorenz curve of $(\boldsymbol{p}, \boldsymbol{q})$ can be graphically represented alongside two divergences: $D_0(\boldsymbol{p}\|\boldsymbol{q})$ and $D_\infty(\boldsymbol{p}\|\boldsymbol{q})$, where $e^{D_0(\boldsymbol{p}\|\boldsymbol{q})} = \sum_{i:p_i>0} q_i$ and $e^{-D_\infty(\boldsymbol{p}\|\boldsymbol{q})} = \max_i\{\frac{p_i}{q_i}\}$

Theorem 12 (Conditions for state conversion). *1. If $(\boldsymbol{p}, \boldsymbol{q}) \succ (\tilde{\boldsymbol{p}}, \tilde{\boldsymbol{q}})$, then*

$$D_0(\boldsymbol{p}\|\boldsymbol{q}) \geq D_0(\tilde{\boldsymbol{p}}\|\tilde{\boldsymbol{q}}) \qquad D_\infty(\boldsymbol{p}\|\boldsymbol{q}) \geq D_\infty(\tilde{\boldsymbol{p}}\|\tilde{\boldsymbol{q}}) \tag{1.88}$$

2. $(\boldsymbol{p}, \boldsymbol{q}) \succ (\tilde{\boldsymbol{p}}, \tilde{\boldsymbol{q}})$ holds, if

$$D_0(\boldsymbol{p}\|\boldsymbol{q}) \geq D_\infty(\tilde{\boldsymbol{p}}\|\tilde{\boldsymbol{q}}) \tag{1.89}$$

Proof. These are obvious from Fig. 1.2. We note that statement 1 is nothing but the monotonicity of $D_0(\boldsymbol{p}\|\boldsymbol{q})$ and $D_\infty(\boldsymbol{p}\|\boldsymbol{q})$, as shown in theorem 11 □

We shall conclude this section with a special case of relative majorization called *thermomajorization*. This is a crucial building block for the resource theory of thermodynamics. Consider a relative majorization $(\boldsymbol{p}, \boldsymbol{q}) \succ (\tilde{\boldsymbol{p}}, \tilde{\boldsymbol{q}})$ such that $\boldsymbol{q} = \tilde{\boldsymbol{q}}$. Such a relative majorization is referred to as thermomajorization.

From the definition 16 of relative majorization, we know that $\boldsymbol{q}$ have full rank. Moreover, any full rank classical state $\boldsymbol{q}$ can be understood as classical state that arises from the diagonal elements of a *Gibbs state* with some Hamiltonian i.e.,

$$\begin{aligned} &\forall \boldsymbol{q} \in \mathcal{P}_d \quad \text{with rank}(\boldsymbol{q}) = d \quad \exists \text{ Hamiltonian } H \text{ and inverse temperature } \beta > 0 \\ &\text{such that} \quad \boldsymbol{q} = \text{Diag}\left(\frac{e^{-\beta H}}{\text{Tr} e^{-\beta H}}\right) \end{aligned} \tag{1.90}$$

that justifies the name thermomajorisation. Thus, we shall define formally thermomajorization as

Definition 18 (Thermomajorization)**.** Let $\boldsymbol{p},\ \tilde{\boldsymbol{p}},\ \boldsymbol{q}$ are d-dimensional classical state. We say $\boldsymbol{p}$ thermomajorizes $\tilde{\boldsymbol{p}}$ if $(\boldsymbol{p},\boldsymbol{q}) \succ (\tilde{\boldsymbol{p}},\boldsymbol{q})$.

We shall talk about thermo-majorization in more detail in the next chapter to describe thermal operations. In the next section, we shall talk about majorization and relative majorization in presence of a catalyst.

1.5 Catalytic Majorization

In this section, we shall discuss majorization in presence of a catalyst. The concept of catalytic majorization involves the idea of a catalyst, a classical state that enables the transformation of a quantum state into another state, and provides necessary and sufficient conditions of the extent to which one state can be transformed into another with the help of a catalyst.

Definition 19 (Catalytic Majorization)**.** Consider $\boldsymbol{p}$ and $\tilde{\boldsymbol{p}}$ are classical states in d-dimension. We say that $\boldsymbol{p}$ catalytically majorizes $\tilde{\boldsymbol{p}}$, or $\boldsymbol{p}$ trumped into $\tilde{\boldsymbol{p}}$, if there is a classical state $\boldsymbol{c} \in \mathcal{P}_{d_C}$ such that

$$\boldsymbol{p} \otimes \boldsymbol{c} \succ \tilde{\boldsymbol{p}} \otimes \boldsymbol{c}. \tag{1.91}$$

We shall show a non-trivial example of trumping. Consider classical state $\boldsymbol{p}$ and $\tilde{\boldsymbol{p}}$

$$\boldsymbol{p} = \left(\frac{4}{10}\ \frac{4}{10}\ \frac{1}{10}\ \frac{1}{10}\right)^T \quad ; \quad \tilde{\boldsymbol{p}} = \left(\frac{1}{2}\ \frac{1}{4}\ \frac{1}{4}\ 0\right)^T \quad ; \quad . \tag{1.92}$$

One can check easily that $\boldsymbol{p} \succ \tilde{\boldsymbol{p}}$ does not hold. But $\boldsymbol{p}$ can be trumped into $\tilde{\boldsymbol{p}}$ with the aid of a catalyst $\boldsymbol{c}$ is given by

$$\boldsymbol{c} = \left(\frac{6}{10}\ \frac{4}{10}\right). \tag{1.93}$$

The necessary and sufficient condition for catalytic majorization or trumping is proven in [51, 52] that can be stated as follows.

Theorem 13. *Consider $\boldsymbol{p}$ and $\boldsymbol{q}$ are classical states with full rank in d-dimensions, and $\boldsymbol{p}^{\downarrow} \neq \boldsymbol{q}^{\downarrow}$.*

Then, it is possible to transform $\mathbf{p}$ *into* $\boldsymbol{q}$ *if and only if* $f_\alpha(\boldsymbol{p}) > f_\alpha(\boldsymbol{q})$ *for all* $\alpha \in (-\infty, +\infty)$*, where*

$$f_\alpha(\boldsymbol{p}) = \left\{ \begin{array}{ll} \log\left(\sum_i p_i^\alpha\right), & \text{for } \alpha > 1 \\ \sum_i p_i \log p_i, & \text{for } \alpha = 1 \\ -\sum_i \log p_i, & \text{for } \alpha = 0 \\ -\sum_i \log p_i, & \text{for } \alpha = 0 \\ \log\left(\sum_i p_i^\alpha\right), & \text{for } 0 < \alpha < 1 \\ -\sum_i \log p_i, & \text{for } \alpha < 0 \end{array} \right\} \tag{1.94}$$

The statement in theorem 13 is that f_α is equal to the Renyi α-entropy (including negative α) up to a negative coefficient, except for $\alpha = 0$. To obtain the Renyi 0-entropy, a slight deviation in the final state is allowed for the $\alpha = 0$ case.

Lemma 14 (Proposition 4 of [34])**.** *Consider the classical state* $\boldsymbol{p}, \tilde{\boldsymbol{p}} \in \mathcal{P}_d$ *. Then, the following are equivalent.*

1. *For all* $\delta > 0$*, there is a classical state* $\tilde{\boldsymbol{p}}_\delta$ *such that* $\tilde{\boldsymbol{p}}$ *can be trumped into* $\tilde{\boldsymbol{p}}_\delta$ *such that* $D(\tilde{\boldsymbol{p}}, \tilde{\boldsymbol{p}}_\delta) \leq \delta$.
2. $H_\alpha(\boldsymbol{p}) \geq H_\alpha(\tilde{\boldsymbol{p}})$ *holds true for all* $\alpha \in (-\infty, +\infty)$.

In [34], authors present an alternative definition of approximate trumping, in which the required and sufficient condition is given by $H_\alpha(\boldsymbol{p}) \leq H_\alpha(\tilde{\boldsymbol{p}})$ but only for α values ranging from 1 to ∞.

Definition 20 (Relative catalytic majorization)**.** Consider the classical states $\boldsymbol{p}, \boldsymbol{q}, \tilde{\boldsymbol{p}}, \tilde{\boldsymbol{q}} \in \mathcal{P}_d$. We say that $(\boldsymbol{p}, \boldsymbol{q})$ relatively majorizes $(\tilde{\boldsymbol{p}}, \tilde{\boldsymbol{q}})$ with the assistance of a catalyst if there exist d' dimensional classical states $\boldsymbol{b}, \boldsymbol{c}$ such that

$$(\boldsymbol{p} \otimes \boldsymbol{b}, \boldsymbol{q} \otimes \boldsymbol{c}) \succ (\tilde{\boldsymbol{p}} \otimes \boldsymbol{b}, \tilde{\boldsymbol{q}} \otimes \boldsymbol{c}). \tag{1.95}$$

In the above definition, it is often possible to take $\boldsymbol{b}$ and $\boldsymbol{c}$ as the uniform classical state $\boldsymbol{u}$. In the case of thermomajorization, this implies the Hamiltonian of the catalyst is trivial.

The theorem 9 can be further generalized to the following form.

Theorem 15 (Theorem 17 of [34])**.** *Let* $\boldsymbol{p}, \boldsymbol{q}, \tilde{\boldsymbol{p}}, \tilde{\boldsymbol{q}} \in \mathcal{P}_d$ *are full rank classical states. Then the following statements are equivalent.*

1. *For any* $\delta > 0$*, there exists a classical state* $\boldsymbol{p}'_\delta \in \mathcal{P}_d$ *such that* $(\boldsymbol{p}, \boldsymbol{q})$ *relatively catalytically majorizes* $(\tilde{\boldsymbol{p}}_\delta, \tilde{\boldsymbol{q}})$ *such that* $D_{Tr}(\tilde{\boldsymbol{p}}, \boldsymbol{p}_\delta) \leq \delta$.
2. $D_\alpha(\boldsymbol{p} \| \boldsymbol{q}) \leq D_\alpha(\tilde{\boldsymbol{p}} \| \tilde{\boldsymbol{q}})$ *for all* $\alpha \in (-\infty, +\infty)$.

Moreover, the classical state of the catalyst can be taken as a uniform state.

The above theorem implies that the α-divergences with $-\infty < \alpha < +\infty$ constitute a complete set of monotones in the presence of a catalyst.

If we remove the constraint that the catalyst must return to its initial state without any correlation with the system, the characterization of state convertibility changes significantly. According to [53], any state conversion is achievable when this requirement is absent, regardless of the system and catalyst sizes, provided that the error in the final state is negligible and unrelated to their sizes. In other words, the presence of a non-exact catalyst causes the majorization structure to become trivial, resulting in what is known as the embezzling phenomenon. In the domain of thermodynamics [34], this phenomenon suggests that an auxiliary system whose operation is not precisely cyclic can be "embezzled" to surpass the standard thermodynamic limit and produce more work.

Theorem 16 (Main result of [53])**.** *For any $\delta > 0$ and any classical states $\boldsymbol{p}, \boldsymbol{q} \in \mathcal{P}_d$, there exists a catalyst in the state $\boldsymbol{c} \in \mathcal{P}_{d'}$ and a classical state $\boldsymbol{r} \in P_{dd'}$ such that $\boldsymbol{p} \otimes \boldsymbol{c} \succ \boldsymbol{r}$ and $D_{Tr}(\boldsymbol{r}, \boldsymbol{q} \otimes \boldsymbol{c}) < \delta$.*

It has been established that there are various ways to create a nontrivial non-exact majorization structure by modifying the setup from the embezzling phenomenon. In this scenario, we assume that the change in the catalyst state is almost exact. Interestingly, the KL divergence is often a single complete monotone for such setups, as explained below. Consequently, when there is such a modestly non-exact catalyst present, the standard KL divergence can entirely characterize thermodynamic transformation. In [34] it was demonstrated that if the approximation error is modestly scaled with the dimension of the catalyst, then the majorization condition is only determined by the Shannon entropy with small correction terms.

Theorem 17. *Let us consider classical state $\boldsymbol{p}, \tilde{\boldsymbol{p}} \in \mathcal{P}_d$.*

1. *Let $\delta \geq 0$. If there exist a classical state $\boldsymbol{r} \in \mathcal{P}_N$ of a catalyst and a classical state $\tilde{\boldsymbol{r}} \in P_{dN}$ such that $\tilde{\boldsymbol{r}} \prec \boldsymbol{p} \otimes \boldsymbol{r}$ and $D_{Tr}(\tilde{\boldsymbol{r}}, \tilde{\boldsymbol{p}} \otimes \boldsymbol{r}) \leq \frac{\delta}{2 \ln N}$, then*
$$H(\boldsymbol{p}) \leq H(\tilde{\boldsymbol{p}}) - \left(\delta + \frac{\delta}{\ln d} + h\left(\frac{\delta}{\ln N}\right)\right), \tag{1.96}$$
where $h(x) := -x \ln x - (1-x)\ln(1-x)$ is the binary entropy function.
2. *If $H(\boldsymbol{p}) < H(\tilde{\boldsymbol{p}})$, then for any sufficiently large N, there exist a classical state $\boldsymbol{r} \in P_N$ of a catalyst and a classical state $\tilde{\boldsymbol{r}} \in P_{dN}$ such that $\tilde{\boldsymbol{r}} \prec \boldsymbol{p} \otimes \boldsymbol{r}$ and $D_{Tr}(\tilde{\boldsymbol{r}}, \tilde{\boldsymbol{p}} \otimes \boldsymbol{r}) \leq \exp(-c \ln N)$ for some constant $c > 0$.*

Now we will explore a situation where several subsystems within the catalyst can generate correlations in the ultimate state [54, 55]. Consequently, the autonomy of the subsystems within the catalyst can be utilized as a means of transforming the state. The following theorem serves as an instance of the majorization case (for the thermo-majorization case, refer to theorem 1 in [54]).

Theorem 18. *(Theorem 1 of [55]) Consider classical states $\boldsymbol{p}, \tilde{\boldsymbol{p}} \in P_d$ with $\boldsymbol{p}^{\downarrow} \neq \tilde{\boldsymbol{p}}^{\downarrow}$. The following are equivalent:*

1. *There exist classical state $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_k \in \mathcal{P}_N$ of a k-partite catalyst and a distribution $\boldsymbol{r} \in P_{kN}$ with marginals $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_k$ such that $\tilde{\boldsymbol{p}} \otimes \boldsymbol{r} \prec \boldsymbol{p} \otimes \boldsymbol{r}_1 \otimes \boldsymbol{r}_2 \otimes \cdots \otimes \boldsymbol{r}_k$.*
2. *$H_0(\boldsymbol{p}) \leq H_0(\tilde{\boldsymbol{p}})$ and $H(\boldsymbol{p}) < H(\tilde{\boldsymbol{p}})$ hold.*

Moreover, one can choose $k = 3$.

Finally, we briefly examine the case where a limited amount of correlation between the system and the catalyst is permitted in the final state, while the catalyst's marginal state must remain identical to the initial state. This transformation is known as *correlated-catalytic transformation* [56, 57].

Theorem 19. *Consider classical state $\boldsymbol{p}, \tilde{\boldsymbol{p}} \in \mathcal{P}_d$ with $\boldsymbol{p} \neq \tilde{\boldsymbol{p}}$. The following are equivalent:*

1. *There exists a distribution $\boldsymbol{r} \in \mathcal{P}_N$ of a catalyst and a classical state $\tilde{\boldsymbol{r}} \in P_{dN}$ such that $\tilde{\boldsymbol{r}} \prec \boldsymbol{p} \otimes \boldsymbol{r}$ and the marginal classical state of $\tilde{\boldsymbol{r}}$ equal $\tilde{\boldsymbol{p}}$ and $\boldsymbol{r}$.*
2. *The inequalities $H_0(\boldsymbol{p}) \leq H_0(\tilde{\boldsymbol{p}})$ and $H(\boldsymbol{p}) < H(\tilde{\boldsymbol{p}})$ satisfies.*

   Moreover, for any $\delta > 0$, one can take $\tilde{\boldsymbol{r}}$ with which the mutual information between the system and the catalyst is smaller than δ.

This theorem has further been extended to relative majorization in theorem 1 of [58], and to approximate relative majorization, as demonstrated in theorem 7 of [59] and theorem 2 of [58]. Notably, the characterization of approximate relative majorization is solely based on the KL divergence.

Theorem 20. *Let $\boldsymbol{p}, \tilde{\boldsymbol{p}}, \boldsymbol{q}, \tilde{\boldsymbol{q}} \in \mathcal{P}_d$ are classical states and suppose that $\boldsymbol{q}, \tilde{\boldsymbol{q}}$ have full rank. Then, the following statements are equivalent.*

1. *For any $\delta > 0$, there exist a classical state $\tilde{\boldsymbol{p}}_\delta \in \mathcal{P}_d$, and a classical state $\boldsymbol{r}_\delta, \boldsymbol{s} \in \mathcal{P}_N$ of a catalyst, and a classical state $\tilde{\boldsymbol{r}}_\delta \in \mathcal{P}_{dN}$, such that $(\tilde{\boldsymbol{r}}_\delta, \boldsymbol{q} \otimes s) \prec (\boldsymbol{p} \otimes \boldsymbol{r}_\delta, \boldsymbol{q} \otimes \boldsymbol{s})$, the marginals of $\tilde{\boldsymbol{r}}_\delta$ equal $\tilde{\boldsymbol{p}}_\delta$ and $\boldsymbol{r}_\delta$, and $D_{\mathrm{Tr}}(\tilde{\boldsymbol{p}}, \tilde{\boldsymbol{p}}_\delta) \leq \delta$.*
2. *$D(\boldsymbol{p} \| \boldsymbol{q}) \leq D(\tilde{\boldsymbol{p}} \| \tilde{\boldsymbol{q}})$ holds.*

Moreover, in statement 1, we can take $\boldsymbol{s}$ as the uniform classical state $\boldsymbol{u}$. Also, for all $\delta > 0$, one can take $\tilde{\boldsymbol{r}}_\delta$ (for a given δ) for which the mutual information between the system and the catalyst is smaller than δ.

This above-stated theorem 20 can be readily extended to the quantum setting, where quantum majorization is considered [59, 60]. The quantum version of theorem 19 has also been established [54], with the catalyst state (denoted as $\boldsymbol{s}$ in the classical case) being set to a uniform classical state. The proof in [54] employs the asymptotic settings where the KL divergence appears as a single complete monotone.

Chapter 2

Resource theory of athermality

2.1 Introduction

The term *resource* refers to a quantity that is useful for accomplishing tasks by an *agent* that is limited by certain physical constraints. An agent with unlimited power and no physical limitations would not recognize anything as a resource. For instance, a hypothetical user who can transmit signals faster than the speed of light would not view digital communication systems as a resource. In the real world, where we cannot transmit signals faster than the speed of light, digital communication systems are an essential resource for sending messages. Similarly, if the objective is to store information obtained from a source, the size of the memory becomes a relevant resource.

Resource theories are abstract mathematical framework inspired by information theory that enables the quantification and management of resources. In a laboratory experiment where an agent is limited in performing certain types of operations, any quantity that cannot be created from these operations is considered a resource. Therefore, a general resource theory is determined by two fundamental elements:

1. *Free Operations:* A set of operations that can be executed without incurring any costs.
2. *Free States:* A set of states that can be generated and used without any costs.

States that are not free are identified as *resources*. Therefore, a specific resource theory is fully characterized by specifying the set of free operations and free states.

In this thesis, we are concerned with the resource theory of thermodynamics described in the quantum mechanical framework. The central question that is addressed in the quantum resource theoretic framework often referred to as *state interconversion problem* is the following:

If an agent is given with a quantum state ρ, what are the set of states the agent can access from ρ employing the free states and free operations only? In a broader aspect, the state interconversion problem has been studied mainly in three different regimes for different resource theory:

1. The *asymptotic regime*, which deals with the problem when an infinitely large number of copies of initial states are available [39, 35, 61, 62].
2. The *single shot regime*, which takes into account only a single copy of the initial state [33, 34, 44].
3. The *intermediate regime*, where the state interconversion problem is addressed when a finitely large number of copies of initial states are available [63]. In chapter 3 of the thermodynamic framework, we will examine the state interconversion problem in this regime.

That motivates to characterize the set of necessary and sufficient conditions for state interconversion problem i.e., the state ρ can be converted to σ using free operations if and only if a functions forming a particular set $\{f_i\}$ decrease in the transition i.e., $\rho \xrightarrow{\text{Free}} \sigma \quad \Leftrightarrow \forall i \quad f_i(\rho) \geq f_i(\sigma)$. The set $\{f_i\}$ is referred to as the *complete set of monotones*.

An example of a resource theory in quantum information involves identifying entanglement between quantum states as a valuable resource. The scenario involves two experimenters, Alice and Bob, located in separate labs A and B, respectively. Alice and Bob are permitted to create any local quantum state and perform any arbitrary complete positive trace non-increasing transformation on the state in their respective labs. Additionally, they can communicate with each other via a classical channel, such as a telephone. These constraints constitute a set of operations referred to as local operation assisted with classical communication (LOCC) transformation. According to [64, 65, 66, 67, 68, 69], entanglement cannot be created using LOCC transformation. Therefore, the combined state of Alice and Bob is separable, and any a priori shared entangled state is deemed a valuable resource. Shared entanglement, when combined with classical communication, can be employed to execute *teleportation*, the transfer of a quantum state. Thus, the resource theory of entanglement is established with a separable state as a free state and LOCC operations as free operations.

Prior to introducing the resource theoretic framework of thermodynamics, let us first provide an overview of the underlying structures of different resource theories. Table 2.1, taken from chapter 26 of [32], presents the key characteristics of various quantum resource theories.

Although entanglement theory has been widely studied, its mathematical framework shares many similarities with other resource theories, enabling researchers to extend results across different domains. In the case of entanglement resource theory, for instance, the set of local operation assisted with classical communication (LOCC) operations is considered

Resource theory	Free Operations	Free states	State interconvertibility condition
Entanglement Theory (Bipartite)	LOCC Operations	Any separable state $\rho_{\text{sep}} = \sum_i p_i \rho_i^A \otimes \rho_i^B$	$\lvert\psi\rangle \xrightarrow{LOCC} \lvert\phi\rangle \Leftrightarrow$ $\text{Eig}(\text{Tr}_A(\lvert\phi\rangle\langle\phi\rvert)) \succ \text{Eig}(\text{Tr}_A(\lvert\psi\rangle\langle\psi\rvert)$ This condition implies that $S(\text{Tr}_A(\lvert\phi\rangle\langle\phi\rvert) \geq S(\text{Tr}_A(\lvert\psi\rangle\langle\psi\rvert)$ where $S(\,\cdot\,)$ denotes the von Neumann entropy which is a monotone.
Asymmetry w.r.t a fixed group G	CPTP map T_G such that for any unitary representation of G $\forall g \in G\ ,\ T_G\Big[U_g(\,\cdot\,)U_g^\dagger\Big]$ $= U_g T_G(\,\cdot\,)U_g^\dagger$	Any state ρ such that $\forall U_g\ ,\quad U_g \rho U_g^\dagger = \rho$	$\rho \to \sigma$ only if $\text{Sym}_G(\rho) \subseteq \text{Sym}_G(\sigma)$ where $\text{Sym}_G(\rho) =$ $\Big\{g \in G\ :\ U_g \rho U_g^\dagger = \rho\Big\}$ and $\text{Sym}_G(\sigma) =$ $\Big\{g \in G\ :\ U_g \sigma U_g^\dagger = \sigma\Big\}$
Coherence in a fixed basis $\{\lvert j\rangle\}_{j=1}^d$	Incoherent operation Λ s.t $\Lambda(\rho) \in \mathcal{I}$ where $\mathcal{I}$ is the set of states that are diagonal in the basis $\{\lvert j\rangle\}_{j=1}^d$	Any $\rho \in \mathcal{I}$ diagonal in the basis $\{\lvert j\rangle\}_{j=1}^d$	$\rho \to \sigma$ only if $C_{\text{RE}}(\rho) \leq C_{\text{RE}}(\sigma)$ where $C_{\text{RE}}(\rho) = \text{min}_{\delta\in\mathcal{I}} D(\rho\Vert\delta)$. Here $D(\rho\Vert\delta)$ is KL divergence $D(\rho\Vert\delta) = \text{Tr}[\rho(\text{log}\rho - \text{log}\sigma)]$
Purity	Unitary operations	Maximally mixed state $\frac{\mathbb{I}}{d}$	Majorization: $\rho \to \sigma$ iff $\text{Eig}(\rho) \succ \text{Eig}(\sigma)$
Thermodynamics	Energy conserving unitary operation	Thermal state γ_S at inverse temperature β	Thermo-majorization: we shall discuss this in detail

Table 2.1: This table is taken from chapter 26 of [32] that summarizes the structure of different resource theory

as free operations, while separable states are regarded as free states. Consequently, any state that contains entanglement is considered a valuable resource. In the upcoming sections, we will outline the fundamental components of the thermodynamic resource theory framework.

2.2 Resource theory of athermality

After introducing the generic resource theory framework, we will now establish the resource theoretic framework of athermality [33, 70, 71]. The goal of this theory is to provide a comprehensive and precise approach to understanding state transformations in a manner that is *thermodynamically free*. To clarify, we will define what we mean by the phrase *ther-*

modynamically free and identify the operations that qualify as free in the resource theory of athermality. The natural and straightforward answer to this question is operations that adhere to the laws of thermodynamics. For instance, in classical equilibrium thermodynamics, we consider a box filled with an ideal gas possessing internal energy U, volume V, and a number of particles N, in contact with a heat bath at temperature T. These three variables determine the equilibrium state, which we denote as $Y := Y(U, V, N, T)$. A continuous and differentiable function known as entropy or a more general thermodynamic potential S is defined over the set of all equilibrium states. The central question of thermodynamics is to determine the set of accessible equilibrium states from a given state Y. The second law of thermodynamics provides the answer.

$$\text{Equilibrium state } \tilde{Y} \text{ is accessible from } Y \text{ if and only if } S(Y) \leq S(\tilde{Y}). \tag{2.1}$$

The assumption of comparability between equilibrium states, i.e., the idea that either the equilibrium state $\tilde{Y}$ can be reached from Y or vice versa, is often referred to as the comparison hypothesis [11, 12]. However, characterizing accessibility relations in non-equilibrium thermodynamics is considerably more complex task. The absence of a complete order makes it difficult to extend the concept of entropy to non-equilibrium states in a unique way. To develop a resource theory for a non-equilibrium scenario, we must first establish the following:

1. A precise definition of a thermodynamic process that can be formalized within the resource theory framework.
2. A characterization of the partial ordering that emerges in the set of non-equilibrium states, which is determined by the chosen concept of thermodynamic processes. This will involve the refinement of the standard constraint of entropy increase, as presented in Eq. (2.1).

This second point naturally requires the tools from partial ordering that we have described in the previous chapter. We shall use them to build the resource theory of thermodynamics.

After introducing the concept of resource theory and the formalism of state transition in equilibrium thermodynamics, we would like to offer two comments. *Firstly*, it's important to note that the goal of this theory is not to establish a definitive set of axioms, as there are other approaches that may be more suitable for certain practical situations. For instance, resource theory struggles with handling time-varying Hamiltonians and incorporating quantum effects of large-scale systems like phase transitions. *Secondly*, if both the system and bath are small enough to enable a complete solution of their dynamics, then quantum mechanics alone suffices. The resource theory approach is expected to be most valuable in cases where a small number of quantum systems interact with an extensive or, in some cases, an intractable environment. This scenario is relevant to open quantum system dynamics, and we anticipate that the two approaches are interconnected. Although the resource theory approach encompasses some typical master equation treatments, such as Davies maps, it does not rely on a master equation representation and can be viewed as a non-Markovian extension of conventional approaches. The open system approach and resource-theoretical approach differ in the problems they address and the methods they employ. The resource theory approach allows for the quantification of certain thermodynamic properties from a quantum information perspective, seeking new insights into the role of non-equilibrium states as resources for performing tasks. This includes characterizing the structure of non-equilibrium states, utilizing their quantum properties, identifying the optimal strategy for a thermodynamic task, pinpointing quantum advantages, and investigating the intersection between thermodynamics and information theory. This approach can be compared to the resource-theoretical classification and manipulation of entanglement, which complements but does not replace the study of entanglement in many-body systems or experimental generation and manipulation of highly entangled states. While the resource theory approach may have potential applications, its relevance is not yet fully established, and some obstacles still need to be overcome (see the last sections of [32]).

In the next section, we shall proceed to describe the framework of the resource theory of thermodynamics.

2.3 Towards Thermodynamically free operation

The theory of thermodynamics deals with the change of energy and entropy in states when a heat bath is present, as shown in Eq. (2.1). In cases where the heat bath has a completely degenerate Hamiltonian, energy exchange with the heat bath is impossible, and operations involve only changes in entropy. Before delving into the full thermodynamic scenario with various heat baths, it is useful to first examine this simplified model. In the following section, we shall describe the *noisy operations* which can be generalized further to the resource theory of thermodynamics.

2.3.1 Noisy Operation

Definition 21 (Resource theory of purity)**.**

1. Free states are maximally mixed states of arbitrary finite dimension, expressed as $\frac{\mathbb{I}}{d_R}$.
2. Free operations are the so-called *noisy operations*, defined as all unitary transformations followed by a partial trace i.e.,

$$\rho_S \xrightarrow{\mathcal{E}_{\text{Noisy}}} \tilde{\rho}_S \quad \Leftrightarrow \quad \mathcal{E}_{\text{Noisy}}(\rho_S) := \mathrm{Tr}_R\Big[U_{SR}\Big(\rho_S \otimes \frac{\mathbb{I}}{d_R}\Big)U_{SR}^{\dagger}\Big]. \tag{2.2}$$

The concept of *purity* as a resource in the Noisy Operations theory can be easily grasped as the maximum disorder (entropy) is present in free states. This disorder is preserved by unitary transformations and cannot be reduced by partial trace operations. Thus, quantum states with higher purity are considered to be more valuable under noisy operations.

Noisy Operations differs from traditional thermodynamics in that it centers on the information contained in systems rather than energy. It has been accepted as the resource theory of informational nonequilibrium or the resource theory of purity for this reason. Initially presented in [72], this thermodynamic toy model originates from the challenge of eliminating Maxwell's demon [18, 73] and draws inspiration from the resource theory of entanglement manipulations [74, 75, 76, 77]

We would like to highlight two important properties of noisy operations. Firstly, the expectation value of a noisy operation always preserves the maximally mixed state $\rho_S = \frac{\mathbb{I}}{d_S}$, thereby making it an unital channel. Secondly, since all unitary operations can be performed without any cost, it is sufficient to consider the case where both ρ_S and $\tilde{\rho}_S$ are diagonal in the same basis. Let us denote the eigenvalues of ρ_S and $\tilde{\rho}_S$ as classical state or probability vectors $\boldsymbol{p} = \mathrm{Eig}(\rho_S)$ and $\tilde{\boldsymbol{p}} = \mathrm{Eig}(\tilde{\rho}_S)$, respectively.

Now we are going to establish an equivalence between the noisy operation and probabilistic mixing of the elements of $\boldsymbol{p}$ in the following theorem:

Theorem 21. *The following statements are equivalent:*

1. *There exists a Noisy operation $\mathcal{E}_{\text{Noisy}}$ such that $\mathcal{E}_{\text{Noisy}}(\rho_S) = \tilde{\rho}_S$.*
2. *There exists a Bistochastic matrix B_{Noisy} such that $B_{\text{Noisy}}\boldsymbol{p} = \tilde{\boldsymbol{p}}$.*

Proof. The proof straightforwardly emerges as a special case of theorem 22. We shall discuss about this after the proof of theorem 22. □

This theorem 21 tells us that the state transition conditions for noisy operations dependent solely on the eigenvalues of initial and target quantum states. Moreover, employing theorem 9, we can say $\boldsymbol{p} \succ \tilde{\boldsymbol{p}}$ since $B_{\text{Noisy}}\boldsymbol{p} = \tilde{\boldsymbol{p}}$. In addition, the theorem 9 implies that von Neumann entropy of the state ρ_S is a monotone under noisy operation since $\boldsymbol{p} \succ \tilde{\boldsymbol{p}}$, we have

$$S(\rho_S) := -\mathrm{Tr}(\rho_S \log \rho_S) = H(\boldsymbol{p}) \geq H(\tilde{\boldsymbol{p}}) = -\mathrm{Tr}(\tilde{\rho} \log \tilde{\rho}) = S(\tilde{\rho}_S), \tag{2.3}$$

where $S(\cdot)$ and $H(\cdot)$ are von Neumann and Shannon entropy and the inequality follows from Eq. (1.12). More generally any α-Renyi entropy is non-decreasing under noisy operation. This follows from statement 3 of theorem 9 simply by taking $f(\cdot) = (\cdot)^{\alpha}$. In a nutshell, the condition that ρ_S can be transformed into $\tilde{\rho}_S$ via noisy operations, therefore, boils down to a simple condition about the classical states:

$$\tilde{\rho}_S = \mathcal{E}_{\text{Noisy}}(\rho_S) \quad \iff \quad \boldsymbol{p} \succ \tilde{\boldsymbol{p}}. \tag{2.4}$$

To conclude this section, we would like to note that for any initial state ρ_S, simulating the full range of possible transformations via noisy operations requires the ancilla dimension d_R to be as large as d_S [78]. In the next section, we will build upon this framework of noisy operations and consider a scenario where a non-trivial heat bath is present, enabling energy exchange between the system and its environment. This will allow us to describe thermodynamically free transformations, also referred to as *thermal operations*.

2.3.2 Motivation and formulation of resource theory of athermality

The maximally mixed state, which serves as the free state of the resource theory of purity, possesses unique characteristics. It exhibits the highest von Neumann entropy and is invariant under any noisy operation, resembling the concise formulation of the second law of classical thermodynamics that dictates the impossibility of a decrease in entropy/disorder in an isolated system. In thermodynamics, the canonical Gibbs ensemble results from a statistical inference that assumes maximum entropy due to a lack of knowledge regarding the system state, under the constraints of known macroscopic variables or conserved quantities such as the average total energy. In scenarios where the Hamiltonian of the system is completely degenerate and all microstates have the same energy, the maximally mixed state becomes equivalent to the Gibbs state. Having established this, we will now introduce the resource theory of athermality.

Definition 22 (Resource theory of athermality)**.** Resource theory of athermality is formulated by taking

1. *Free state* as Gibbs state of the system at the temperature of the heat bath i.e.,

$$\gamma_S = \frac{e^{-\beta H_S}}{\mathrm{Tr}(e^{-\beta H_S})}, \tag{2.5}$$

   where H_S is the Hamiltonian of the system and $\beta = \frac{1}{k_B T}$.

2. *Free operation* as *thermal operation* which is defined as follows:

$$\mathcal{E}(\rho) = \mathrm{Tr}_E\Big[U(\rho \otimes \gamma_B)U^\dagger\Big], \tag{2.6}$$

   where H_B is the Hamiltonian of the bath and U is an energy-conserving unitary is th i.e., $[U, H_S + H_B] = 0$, and

$$\gamma_B = \frac{e^{-\beta H_B}}{Z_B}. \tag{2.7}$$

Thus resource theoretic framework addresses the following question: *What is the set of final states attinable from a given initial state through thermal operation?*.

Below we present a motivation for the formulation of resource theory of athermality.

Why the Gibbs state of the system only considered as free state in the framework? The proposed framework defines free states as those that can be prepared without consuming any work in the presence of an environment at temperature T. A Gibbs state at temperature $T' \neq T$ can generate heat flow that can be exploited to extract work, whereas a Gibbs state at temperature T does not generate any heat flow. Therefore, any Gibbs state that is not at the temperature of the environment can be seen as a resource. To formalize this argument, let us consider a system S with Hamiltonian H_S in thermal equilibrium with its surrounding environment at temperature T. The state of the system, γ_S, can be expressed as

$$\gamma_S = \frac{e^{-\beta H_S}}{\text{Tr}(e^{-\beta H_S})}. \tag{2.8}$$

We argue that only γ_S can be considered a free state. Suppose σ_S is another free state such that $\sigma_S \neq \gamma_S$. This implies that N copies of σ_S, denoted as $\sigma_S^{\otimes N}$, can also be prepared without any work for arbitrary values of N. However, it can be shown that there exist sufficiently large values of N for which $\sigma_S^{\otimes N}$ is *active*. This means that it is possible to extract work from it via a unitary transformation. More specifically, there exists a unitary U such that

$$\text{Tr}(H_S^{(N)} \sigma_S^{\otimes N}) - \text{Tr}(H_S^{(N)} U \sigma_S^{\otimes N} U^\dagger) > 0, \tag{2.9}$$

where $H_S^{(N)} = \sum_{i=1}^{N} H_{S,i}$ with $H_{S,i} = \mathbb{I}_1 \otimes \ldots \otimes \mathbb{I}_{i-1} \otimes H_S \otimes \mathbb{I}_{i+1} \otimes \mathbb{I}_N$. The unitary U can be understood as being generated due to a time-dependent Hamiltonian that starts in $H_S^{(N)}$ at the beginning of the protocol and returns $H_S^{(N)}$ at the end. The drop in energy, $\text{Tr}(H_S^{(N)} \sigma_S^{\otimes N}) - \text{Tr}(H_S^{(N)} U \sigma_S^{\otimes N} U^\dagger)$, can be stored as work in the form of an increment in the average energy of a harmonic oscillator. This argument naturally extends to the fact that the preparation of an active state requires some work and thus cannot be considered free [79]. On the other hand, for any arbitrary values of N, $\gamma_S^{\otimes N}$ is not active and can be considered free. It is well-known from [40] that it is possible to extract work from an active state, while a passive state cannot generate any work. Further discussion of active and passive states will be provided in chapter 3.

Why only energy conserving unitaries are considered to be free? We will now describe the reason why only energy-conserving unitaries are regarded as free operations. This is motivated from the first law of thermodynamics. Systems are described by quantum states, and as such, their evolution should be described by unitary evolutions U across the closed system S and environment E. Additionally, the thermodynamic process described must preserve energy over the entire system that demands

$$[U, H_S + H_B] = 0. \tag{2.10}$$

On the other hand, suppose we consider a unitary operation, denoted as V, that does not conserve energy. In such a scenario, the action of the non-energy-conserving unitary V on the state $\gamma_S \otimes \gamma_B$ can be expressed as follows:

$$V(\gamma_S \otimes \gamma_B)V^\dagger \neq \gamma_S \otimes \gamma_B. \tag{2.11}$$

Hence, unitary V can generate several copies of athermal states by acting on $(\gamma_S \otimes \gamma_B)^{\otimes N}$, leading to the preparation of an active state when N is sufficiently large. As previously noted, work can be extracted from active states, thereby allowing any arbitrary unitary V to be considered a free operation in the framework, leading to the creation of active states for free. To prevent this, we require $V(\gamma_S \otimes \gamma_B)V^\dagger = \gamma_S \otimes \gamma_B$. This can be rewritten as

$$\begin{aligned} & Ve^{-\beta(H_S+H_B)}V^\dagger = e^{-\beta(H_S+H_B)} \quad \Rightarrow e^{-\beta V(H_S+H_B)V^\dagger} = e^{-\beta(H_S+H_B)} \\ \Rightarrow \quad & [V, H_S + H_B] = 0. \end{aligned} \tag{2.12}$$

Here, the equation above requires that the commutator of V with the sum of the system and environment Hamiltonians, $H_S + H_B$, must be equal to zero.

In the next section, we would like to describe about the structure of the heat bath that is compatible with the thermal operation.

2.3.3 The structure of heat bath compatible with thermal operation

In many physical contexts, a system exists in the presence of an environment that is a large system in thermal equilibrium. The initial state of the system is generally not in equilibrium with the bath, but the joint dynamics will drive it towards equilibrium. Our objective is to describe this situation using a framework, for which we first need to specify the heat bath or environment that surrounds the system.

In this section, we start by making the assumption that the bath has a limited size [41, 80] and investigate the constraints that come with it. Afterwards, we will explore the limits to take the limit of an infinite size heat baths. To begin with, we shall define the heat bath as follows:

Definition 23 (Heat bath)**.** A heat bath is defined as a large system as compared to system in concern (although not necessarily infinite), described within a Hilbert space $\mathcal{H}_B$. It possesses a effectively continious number of states represented by $g(E, V) = e^{S(E,V)}$, where $S(E, V)$ is the entropy in the microcanonical ensemble for a given energy E and dimensionless volume V (e.g., the total number of particles) such that following assumptions are hold:

1. The entropy $S(E, V)$ is extensive: $S(kE, kV) = kS(E, V)$ for all $k > 0$.
2. The dimensionless volume V is large.
3. The bath is in a Gibbs state with a given inverse temperature β. Therefore, a microstate

of energy E has a probability $\frac{1}{Z_B}e^{-\beta E}$. This indicates that it is in equilibrium with a larger bath.

Let us describe the motivation behind this set of assumptions. We can envision this bath as an extensive system that is a constituent of an even bigger system with an effectively infinite volume. Both systems have been interacting for a longer period of time resulting in thermal equilibrium. However, the interaction time with the system is finite, and it can only interact with a limited but sizable portion of the bath within this time. As a result, we assume that the interactions within the bath possess a light-cone structure, possibly described by Lieb-Robinson bounds, which restrict the rate at which information can propagate through locally interacting many-body systems.

Assumption 1, which states the extensivity of the entropy function, enables us to express the entropy $S(E,V)$ as

$$S(E,V) = Vf(u), \tag{2.13}$$

where $f(u)$ is a function of the energy density $u = \frac{E}{V}$. Consequently, the probability distribution for u can be written as

$$p(u) \propto g(E,V)e^{-\beta E} = e^{S(E,V)}e^{-\beta E} = e^{V(f(u)-\beta u)}. \tag{2.14}$$

In the large V limit, we can employ the saddle-point approximation. Denoting u_β the point at which the function $f(u) - \beta u$ reaches a maximum, we write

$$p(u) \propto e^{V\left(f(u_\beta)+\frac{1}{2}f''(u_\beta)(u-u_\beta)^2\right)}. \tag{2.15}$$

This implies that

$$f'(u_\beta) \quad = \quad \beta, \tag{2.16}$$

$$f''(u_\beta) \quad < \quad 0. \tag{2.17}$$

As $e^{Vf(u_\beta)}$ is a constant on u, we obtain $p(u)$ proportional to a normal distribution with mean $\langle u\rangle = u_\beta$ and variance $\langle (u - \langle u\rangle)^2\rangle = V|f''(u_\beta)|^{-1}$:

$$p(u) \propto e^{-\frac{V}{2}|f''(u_\beta)|(u-u_\beta)^2}. \tag{2.18}$$

We can relate $f''(u_\beta)$ to the heat capacity C that is defined below:

$$C := V\frac{d\langle u\rangle}{dT} = -\frac{V}{T^2}\frac{d\langle u\rangle}{d\beta}. \tag{2.19}$$

By differentiating Eq. (2.16) with respect to β, we obtain $f''(u_\beta)\frac{du_\beta}{d\beta} = 1$, which can be substituted into Eq. (2.19) to give

$$C = -\frac{V}{T^2}\frac{1}{f''(u_\beta)}. \tag{2.20}$$

We note that the heat capacity is positive, as is always the case in ordinary matter. Furthermore, C scales linearly with V since $f(u_\beta)$ is independent of V, which implies that the fluctuations of u are given by

$$\sqrt{\langle (u-\langle u\rangle)^2\rangle} = \frac{T\sqrt{C}}{V} \propto \frac{1}{\sqrt{V}}. \tag{2.21}$$

This expression is small when V is large. Thus we can write the density of states as

$$\begin{aligned} g(E,V) &= e^{S(E,V)} = e^{V\beta u}e^{V\left(f(u)-\beta u\right)} = e^{\beta E}e^{V\left(f(u_\beta)+\frac{1}{2}f''(u_\beta)(u-u_\beta)^2)\right)}, \\ &= e^{\beta E}e^{V\left(f(u_\beta)-\frac{V}{T^2C}(u-u_\beta)^2)\right)}. \end{aligned} \tag{2.22}$$

Denoting $\delta = 1/CT^2$ as the inverse of the heat capacity, we finally obtain

$$g(E,V) \propto e^{(\beta E - \frac{\delta E^2}{2})}. \tag{2.23}$$

We make the assumption that the energy scales of the system interacting with the bath are much smaller than the energy fluctuation of the bath. This assumption is accurate when the bath is sufficiently large, such that for all i we have E_i is smaller than $\frac{1}{\delta}$, where E_i denotes the spectrum of the Hamiltonian of the system. This results the density of states obtained in Eq. (2.23)

$$g(E-E_i) \simeq g(E)e^{-E_i(\beta-\delta E)} \tag{2.24}$$

Considering the limit when volume V of bath goes to ∞ results in infinite heat capacity C as $C \propto V$. This implies $\delta \to 0$ and

$$g(E-E_i) \simeq g(E)e^{-\beta E_i}. \tag{2.25}$$

We shall use this result for the characterization of action of thermal operation on states that are block diagonal in the eigenbasis of H_S.

2.3.4 Thermodynamics of energy incoherent states

The energy eigenbasis, denoted by $\{|E_i\rangle\}_{i=1}^d$, is a significant basis in a d-dimensional Hilbert space. It is given by the eigenstates of the Hamiltonian, $H_S = \sum_{i=1}^d E_i|E_i\rangle\langle E_i|$, which governs the evolution of the system. Any state ρ that is diagonal in this basis will evolve trivially in time under the free evolution of the system, i.e., $e^{-iH_St}\rho e^{+iH_St} = \rho$. These states are known as time-translation invariant states or *energy incoherent states*. This is in sharp contrast to generic quantum states that possess coherence between energy eigenstates, where even complete knowledge about a state may leave one uncertain about its energy. Formally, we thus define the following

Definition 24 (Energy incoherent states)**.** Consider a d- dimensional system described by Hamiltonian $H = \sum_{i=1}^{d} E_i |E_i\rangle\langle E_i|$. A state ρ of a system will be called energy-incoherent if it is diagonal in the energy eigenbasis, i.e., if $\langle E_i|\rho|E_j\rangle = 0$ for all $i \neq j$. Such a state will be equivalently represented by a d-dimensional classical state $\boldsymbol{p} \in \mathcal{P}_d$ with $p_i = \langle E_i|\rho|E_i\rangle$.

Now we would like establish the connection between transformation of energy incoherent state ρ via a thermal operation on one hand, and a transformation of a classical state $\boldsymbol{p}$ under a stochastic matrix which preserves the classical state constructed from Gibbs state of the system on the other hand.

Theorem 22 (Characterization of thermal operations by a Gibbs stochastic matrices [33, 36])**.** *Consider ρ_S and σ_S to be two energy incoherent states i.e., $[\rho_S, H_S] = 0$ and $[\sigma_S, H_S] = 0$ with corresponding classical states $\boldsymbol{p}$ and $\boldsymbol{q}$ constructed from diagonals of ρ_S and σ_S. We denote the $\boldsymbol{\gamma}_S$ as the classical state generated from the diagonal of the Gibbs state of the system $\gamma_S = \frac{e^{-\beta H_S}}{Tr(e^{-\beta H_S})}$. Then the following statements are equivalent:*

1. *There exists a thermal operation $\mathcal{E}$ such that $\sigma_S = \mathcal{E}(\rho_S)$.*
2. *The classical states $\boldsymbol{p}$ and $\boldsymbol{q}$ are related as follows:*

$$\boldsymbol{q} = T^{\mathcal{E}}\boldsymbol{p} \quad ; \quad \boldsymbol{\gamma}_S = T^{\mathcal{E}}\boldsymbol{\gamma}_S, \tag{2.26}$$

where $T^{\mathcal{E}}$ is a stochastic matrix referred as Gibbs stochastic matrix.

Proof. We begin by showing that statement 1 implies statement 2. From $[\rho_S, H_S] = 0$, we can write

$$\rho_S = \sum_{i=1}^{d} p_i |E_i^S\rangle\langle E_i^S|. \tag{2.27}$$

where $\{E_i^S\}_{i=1}^d$ denotes the energy eigenbasis for Hamiltonian H_S. From the defintion of thermal operation given in Eq. (2.6) we can see that $\mathcal{E}$ is trace preserving. Let us define a stochastic matrix $T^{\mathcal{E}}$ as follows:

$$T^{\mathcal{E}}_{(i,j)} := \langle E_j^S|\mathcal{E}\Big(|E_i^S\rangle\langle E_i^S|\Big)|E_j^S\rangle. \tag{2.28}$$

From $\mathcal{E}(\gamma_S) = \gamma_S$ we can check from Eq. (2.28) that $T^{\mathcal{E}}\boldsymbol{\gamma}_S = \boldsymbol{\gamma}_S$. It is straight-forward to check that $T^{\mathcal{E}}$ is a stochastic matrix by adding the elements of the columns for matrix representation $T^{\mathcal{E}}$

$$\forall i, \quad \sum_{j=1}^{d} T^{\mathcal{E}}_{(i,j)} = \sum_{j=1}^{d} \langle E^S_j | \mathcal{E}\Big(|E^S_i\rangle\langle E^S_i| \Big) |E^S_j\rangle = \mathrm{Tr}\Big(\mathcal{E}\Big(|E^S_i\rangle\langle E^S_i| \Big)\Big) = 1. \tag{2.29}$$

where the equality follows from the fact that $\mathcal{E}$ is trace preserving. It is easy to check that

$$\begin{aligned} q_j &= \langle E^S_j|\mathcal{E}(\rho)|E^S_j\rangle = \langle E^S_j|\mathcal{E}\Big(\sum_i p_i |E^S_i\rangle\langle E_i|\Big)|E^S_j\rangle = \sum_i p_i \langle E^S_j|\mathcal{E}(|E^S_i\rangle\langle E^S_i|)|E^S_j\rangle \\ &= \sum_i T^{\mathcal{E}}_{(i,j)} p_i \quad \Rightarrow \quad \boldsymbol{q} = T^{\mathcal{E}} \boldsymbol{p}. \end{aligned} \tag{2.30}$$

The converse is based on an explicit construction of a thermal operation. Since $[\rho_S, H_S] = 0$ then

$$\rho_S = \sum_{i=1}^{d} p_i |E^S_i\rangle\langle E^S_i|. \tag{2.31}$$

Taking Hamiltonian of the bath $H_B = \sum_{j=1}^{d} \sum_{g=1}^{g(E^B_j)} E^B_j |E^B_j\rangle\langle E^B_j|$, where $g(E^B_j)$ is the degeneracy of energy E^B_j, the state of the bath will be

$$\gamma_B = \frac{1}{Z_B} \sum_{j=1}^{d} e^{-\beta E^B_j} \sum_{g=1}^{g(E^B_j)} |E^B_j, g\rangle\langle E^B_j, g|, \tag{2.32}$$

with $Z_B = \mathrm{Tr}(e^{-\beta H_B})$. Then, setting $E = E^S_i + E^B_j$ and summing over E and E^S_i rather than E^S_i and E^B_j we can write $\rho_S \otimes \gamma_B$

$$\begin{aligned} \rho_S \otimes \gamma_B &= \sum_{i=1}^{d} \sum_{j=1}^{d} \sum_{g=1}^{g(E^B_j)} p_i \frac{e^{-\beta E^B_j}}{Z_B} |E^S_i\rangle\langle E^S_i| \otimes |E^B_j, g\rangle\langle E^B_j, g| & (2.33) \\ &= \sum_E \sum_i \sum_{g=1}^{g(E-E^S_i)} p_i \frac{e^{-\beta(E-E^S_i)}}{Z_B} |E, E^S_i, g\rangle\langle E, E^S_i, g|. & (2.34) \end{aligned}$$

Introducing normalisation factor $N(E) = g(E)\frac{e^{-\beta E}}{Z_B}$ and exponential degeneracy (as given in Eq. (2.25)) $D_i(E) := g(E - E^S_i) = g(E)e^{-\beta E^S_i}$, we can rewrite the above as follows:

$$\begin{aligned} \rho_S \otimes \gamma_B &= \sum_E N(E)|E\rangle\langle E| \otimes \sum_i \sum_{g=1}^{D_i(E)} \frac{p_i}{D_i(E)} |E^S_i, g\rangle\langle E^S_i, g| \\ &= \sum_E N(E)|E\rangle\langle E| \otimes \rho_E, \end{aligned} \tag{2.35}$$

where $\rho_E = \sum_i \sum_{g=1}^{D_i} \frac{p_i}{D_i(E)} |E^S_i, g\rangle\langle E^S_i, g|$ are normalised states that encode relative degrees of freedom for a fixed total energy E. Note that thermal operations allow any energy-preserving unitary on every subspace of constant energy E i.e., $\oplus_E U_E$.

Consider the normalized state $\rho_E = \sum_i \sum_{g=1}^{D_i} \frac{p_i}{D_i(E)} |E_i^S, g\rangle\langle E_i^S, g|$. The state ρ_E has groups of $D_i(E)$ copies of each eigenvalue $p_i/D_i(E)$. We chose U_E that are permutations between these groups, moving $N_{i|j}$ eigenvalues from group j to group i. This results the following condition:

$$\sum_{i=1}^{d} N_{i|j} = D_j \quad ; \quad \sum_{j=1}^{d} N_{i|j} = D_i. \tag{2.36}$$

Then the state $\rho_S \otimes \gamma_B$ transformed under such an unitary as

$$\sum_E N(E)|E\rangle\langle E| \otimes U_E \rho_E U_E^\dagger = \sum_E N(E)|E\rangle\langle E| \otimes U_E \Big(\sum_i \sum_j \frac{N_{i|j}(E)}{D_j(E)} p_j |E_i^S, g\rangle\langle E_i^S, g| \Big).g \tag{2.37}$$

We chose

$$\tilde{T}^{\mathcal{E}}_{(i,j)} = \frac{N_{i|j}}{D_j}, \tag{2.38}$$

acting on the classical state $\boldsymbol{p}$. We can check from Eq. (2.36) $\tilde{T}^{\mathcal{E}}$ is stochastic and preserve the classical state constructed from diagonal of γ_S as follows

$$\begin{aligned} &\sum_{i=1}^{d} \tilde{T}^{\mathcal{E}}_{(i,j)} = 1, \\ &\sum_{j=1}^{d} \tilde{T}^{\mathcal{E}}_{(i,j)} \gamma_j = \sum_{j=1}^{d} \frac{N_{i|j}(E)}{D_j(E)} e^{-\beta E_j^S} = \sum_{j=1}^{d} \frac{N_{i|j}(E)}{g(E) e^{-\beta E_j^S}} e^{-\beta E_j^S} = \frac{D_i(E)}{g(E)} = e^{-\beta E_i^S}. \end{aligned} \tag{2.39}$$

Moreover, it is possible to obtain any rational approximation of transition probabilities that generate a Gibbs stochastic matrix by selecting a large enough value for the function $g(E)$. This implies that $\tilde{T}^{\mathcal{E}}$ can be made arbitrarily close to any Gibbs stochastic matrix. To ensure that the Gibbs stochastic matrix is applied within each block of total energy E, we can appropriately choose $D_i(E)$ and $N_{i|j}(E)$ for each E. Consequently, we can conclude that any Gibbs stochastic matrix G can be well approximated by $\tilde{T}^{\mathcal{E}}$ with sufficient accuracy.

□

Now let us analyze some important remarks that follow from this result.

1. *Thermal operation and thermo-majorization correspondence:* Employing theorem 11 we see that for states with $[\rho_S, H_S] = [\sigma_S, H_S] = 0$ we have the following equivalence:

$$\rho_S \xrightarrow{\text{Thermal operation}} \sigma_S \quad \Leftrightarrow \quad \boldsymbol{q} = T^{\mathcal{E}} \boldsymbol{p} \quad ; \quad \gamma_S = T^{\mathcal{E}} \gamma_S \quad \Leftrightarrow \quad (\boldsymbol{p}, \gamma_S) \succ (\boldsymbol{q}, \gamma_S), \tag{2.40}$$

   where $\boldsymbol{p}$ and $\boldsymbol{q}$ constructed from diagonals of ρ_S and σ_S. We defined the relation as thermomajorization in the previous chapter in the definition 18. Therefore, energy incoherent state ρ_S can be transformed to σ_S if and only if classical state $\boldsymbol{p}$ thermomajorizes $\boldsymbol{q}$ i.e., $(\boldsymbol{p}, \boldsymbol{\gamma}_S) \succ (\boldsymbol{q}, \boldsymbol{\gamma}_S)$. Moreover, from theorem 10 of the chapter 1 we see that $(\boldsymbol{p}, \boldsymbol{\gamma}_S) \succ (\boldsymbol{q}, \boldsymbol{\gamma}_S)$ is equivalent to $\Gamma_{\boldsymbol{\gamma}_S}(\boldsymbol{p}) \succ \Gamma_{\boldsymbol{\gamma}_S}(\boldsymbol{q})$ where $\Gamma_{\boldsymbol{\gamma}_S}$ is the embedding map wrt. classical state $\boldsymbol{\gamma}_S$.

2. *Monotonicity properties:* Combining with statement 3 of theorem 11, we obtain if an energy incoherent state ρ can be transformed to energy incoherent state σ then for any real valued convex function f

$$D_f(\boldsymbol{p}\|\gamma) \geq D_f(\boldsymbol{q}\|\gamma). \tag{2.41}$$

where $\boldsymbol{p}$ and $\boldsymbol{q}$ are classical state corresponding to energy incoherent state ρ_S and σ_S. As mentioned earlier, this Eq. (2.41) referred as monotonicity of f-divergence. In particular, we can say that any α- Renyi divergence is a monotone under thermal operation. But this holds true in general as any f-divergence is a monotone under a complete positive trace preserving map.

3. *Noisy operation:* It is straight-foreward to see noisy operation can be realized as a special case of thermal operation considering the Hamiltionian of the bath trivial or fully degenerate. Then the Gibbs state of the bath reduces to $\frac{I}{d}$. Then according to the theorem , in this case 22 we have

$$\mathcal{E}(\rho_S) = \sigma_S \quad \Leftrightarrow \quad T^{\mathcal{E}}(\boldsymbol{p}) = \boldsymbol{q}\ ;\ T^{\mathcal{E}}(\boldsymbol{u}) = \boldsymbol{u}, \tag{2.42}$$

where $\boldsymbol{u}$ is the uniform classical state with all the elements $\frac{1}{d}$. The condition $T^{\mathcal{E}}(\boldsymbol{u}) = \boldsymbol{u}$ implies the matrix $T^{\mathcal{E}}$ is bistochastic. From theorem 9 we can say that $\boldsymbol{p} \succ \boldsymbol{q}$ since $\boldsymbol{q}$ can be obtained from $\boldsymbol{p}$ via bistochastic matrix $T^{\mathcal{E}}$. Hence we have seen theorem 21 as a consequence of theorem 22.

We have establish the abstract framework for thermal operations. In the next section, we shall consider a physical scenario with Jaynes-Cummings interaction that corresponds to thermal operations.

2.3.5 Jaynes Cummings model as a thermal operations

The Jaynes-Cummings model is a quantum mechanical model that describes the interaction between a two-level system, known as a qubit, and a harmonic oscillator, which is typically a cavity or a resonator. One important simplification that is often used in the Jaynes-Cummings model is the rotating wave approximation (RWA). The RWA is a widely used method in quantum optics, which involves neglecting rapidly oscillating terms in the

Hamiltonian. In this essay, we will discuss the RWA and its connection to thermal operations in the qubit Jaynes-Cummings model.

The Jaynes-Cummings Hamiltonian in the most general form is given by

$$H = \frac{1}{2}\omega_0\sigma_z + \omega_c a^\dagger a + g(\sigma_+ + \sigma_-)(a + a^\dagger), \tag{2.43}$$

where a and $a^\dagger$ are the annihilation and creation operators for the harmonic oscillator mode, σ_+ and σ_- are the annihilation and creation operators of qubit, σ_z is the Pauli Z matrix for the qubit. The coupling strength between the qubit and the harmonic oscillator is denoted by g, while ω and ω_0 is the frequencies of the oscillator and the qubit respectively. We denote free Hamiltonian and interaction Hamiltonian as

$$\begin{aligned} H_0 &= \frac{1}{2}\omega_0\sigma_Z + \omega_C a^\dagger a, \\ H_{\text{int}} &= g(\sigma_+ + \sigma_-)(a + a^\dagger). \end{aligned} \tag{2.44}$$

Then in the interaction picture we have the

$$\begin{aligned} e^{-iH_0 t} H_0 e^{+iH_0 t} &= H_0, && (2.45) \\ e^{-iH_0 t} H_{\text{int}} e^{+iH_0 t} &= ig\Big(e^{-i(\omega_C - \omega_0)t} a\sigma_+ + e^{i(\omega_C - \omega_0)t} a^\dagger \sigma_-\Big) \\ &+ ig\Big(e^{-i(\omega_C + \omega_0)t} a\sigma_- + e^{i(\omega_C + \omega_0)t} a^\dagger \sigma_+\Big), && (2.46) \end{aligned}$$

We see the first term in Eq. (2.46) is slowly oscillates whereas second term oscillates faster.The RWA consists of ignoring faster oscillating term $\Big(e^{-i(\omega_C + \omega_0)t} a\sigma_- + e^{i(\omega_C + \omega_0)t} a^\dagger \sigma_+\Big)$ in the Eq. (2.46) which holds if we made the assumption that interaction strength g is smaller than frequency of the qubit ω_0 and the frequency of the oscillator ω_C and $\omega_0 \sim \omega_C$. In this approximation, we can write the interaction Hamiltonian as

$$H_{\text{int}} = \hbar g(\sigma_+ a + \sigma_- a^\dagger). \tag{2.47}$$

The approximation is justified because the rapidly oscillating terms in the original interaction Hamiltonian average out to zero when integrated over a period of the oscillator frequency. The type of interaction in Eq. (2.47) introduces a special symmetry to the problem. Namely, it conserves the number of quanta in the system i.e.,

$$[H, a^\dagger a + \sigma_z] = 0. \tag{2.48}$$

If we assume the resonant condition which is given by $\omega_0 = \omega_C$, we have $[H_0, H_{\text{int}}] = 0$. If $U = e^{-iHt}$ with the Hamiltonian in Eq. (2.43), then under the resonant condition and taking RWA we have $[U, H_0] = 0$. Therefore, this description can be considered as a physical model for transformation of states under thermal operation.

From the GKSL master equation we have [81]

$$\frac{d\rho}{dt} = -i\Big[\frac{\omega_0}{2}\sigma_z, \rho\Big] + \gamma(N+1)\mathcal{D}[\sigma_-] + \gamma(N)\mathcal{D}[\sigma_+], \tag{2.49}$$

with

$$\begin{aligned} N &= \frac{1}{e^{\beta\omega_0}-1} \quad \text{where } \beta = \frac{1}{k_B T}, \\ \mathcal{D}(A) &= A\rho A^\dagger - \frac{1}{2}A^\dagger A, \rho. \end{aligned} \tag{2.50}$$

The Hamiltonian part induces the qubit to precess around the z axis. If there was no dissipation the spin would precess indefinitely. But in the presence of dissipation, it precesses and is also damped towards the z axis. After a long time has elapsed the system will tend to a steady-state, which is the solution of

$$\frac{d\rho}{dt} = 0, \tag{2.51}$$

is given by $\rho_{\text{steady state}} = \begin{pmatrix} \frac{N}{2N+1} & 0 \\ 0 & \frac{N+1}{2N+1} \end{pmatrix}$. This corresponds to a thermal equilibrium density matrix. In the lower temperature limit any thermal operation on a two level system can be realized via Jaynes-Cummings interaction [82]. In the next section, we shall discuss few properties of thermal operation that we shall use in the later parts of this thesis.

2.3.6 Properties of thermal operation

The set of all thermal operations forms a convex set. This can be inferred from the following theorem:

Theorem 23 (Convexity of thermal operations [83])**.** *The set of states that can be achieved via thermal operation from a fixed state ρ forms a convex set.*

Proof. Consider $\sigma_1 = \mathcal{E}_1(\rho)$ and $\sigma_2 = \mathcal{E}_2(\rho)$ where $\mathcal{E}_1$ and $\mathcal{E}_2$ are thermal operation. In order to construct a thermal operation $\mathcal{E}$ such that

$$\mathcal{E}(\rho) = p\sigma_1 + (1-p)\sigma_2 \qquad \forall p \in [0,1]. \tag{2.52}$$

From the definition

$$\mathcal{E}_1(\rho) = \text{Tr}_{E_1} U_1 \left(\rho \otimes \gamma_{E_1}\right) U_1^\dagger \quad \text{where} \quad [U_1, H_S + H_{E_1}] = 0, \tag{2.53}$$

$$\mathcal{E}_2(\rho) = \text{Tr}_{E_2} U_2 \left(\rho \otimes \gamma_{E_2}\right) U_2^\dagger \quad \text{where} \quad [U_2, H_S + H_{E_2}] = 0. \tag{2.54}$$

We introduce a n-dimensional ancillary bath state γ_A with Hamiltonian $H_A = \mathbb{I}_n$ and a joint unitary acting on system, the two environments, and the ancilla. The total Hamiltonian of this joint system is $H = H_S + H_{E_1} + H_{E_2} + H_A$. We introduce the controlled unitary

$$U := \Pi_1 \otimes U_1 + \Pi_2 \otimes U_2, \tag{2.55}$$

where Π_1 and Π_2 is a projector with rank k and $n-k$, respectively and $\Pi_1 + \Pi_2 = \mathbb{I}_n$. We choose k in such a way that $\frac{k}{n}$ is arbitrarily close to p. Thus we have for $i = 1, 2$

$$\begin{aligned} [\Pi_i \otimes U_i, H] &= [\Pi_i \otimes U_i, H_S + H_i] \\ &= \Pi_i \otimes [U_i, H_S + H_i] = 0, \end{aligned} \tag{2.56}$$

which makes $[U, H_S + H_{E_1} + H_{E_2} + H_A] = 0$. We finally have

$$\begin{aligned} & \mathrm{Tr}_{A,E_1,E_2}(U\,(\rho \otimes \gamma_A \otimes \gamma_{E_1} \otimes \gamma_{E_2})\,U^\dagger) \\ = & \frac{1}{n}\sum_{i=1}^{2} \mathrm{Tr}_{A,E_i}[\Pi_i \otimes U_i(\rho \otimes \mathbb{I}_n \otimes \gamma_i)\Pi \otimes U_i^\dagger] \\ = & \frac{k}{n}\mathcal{E}_1(\rho) + (1 - \frac{k}{n})\mathcal{E}_2(\rho). \end{aligned} \tag{2.57}$$

□

Then from the previous theorem we can see the set of achievable states from a fixed state ρ via thermal operation is convex.

Definition 25 (Thermal cone)**.** The set of states that can be achieved via thermal operation from a given state ρ by $\mathcal{T}(\rho)$. This set is called *thermal cone* of the state ρ.

The definition of thermal operation straightforwardly leads to the following two important properties that stated in the following two propositions:

Proposition 24 (Invariance of thermal state under thermal operation)**.** *Let $\mathcal{E}$ be a thermal operation on the system S with Hamiltonian H_S in presence of the bath at inverse temperature. The thermal state of the system*

$$\gamma_S = \frac{e^{-\beta H_S}}{Z_S} \quad where \quad Z_S = Tr(e^{-\beta H_S}), \tag{2.58}$$

is invariant under $\mathcal{E}$ i.e.,

$$\mathcal{E}(\gamma_S) = \gamma_S \tag{2.59}$$

Proof. From the definition of thermal operation $\mathcal{E}$ we can write $\mathcal{E}(\gamma_S)$ as

$$\begin{aligned}\mathcal{E}(\gamma_S) &= \mathrm{Tr}_E\Big(U(\gamma_S\otimes\gamma_B)U^\dagger\Big) = \mathrm{Tr}_E\left[U\Big(\frac{e^{-\beta H_S}}{Z_S}\otimes\frac{e^{-\beta H_B}}{Z_B}\Big)U^\dagger\right] \\ &= \mathrm{Tr}_E\left[U\frac{e^{-\beta(H_S+H_B)}}{Z_SZ_B}U^\dagger\right] = \mathrm{Tr}_E\left[\frac{e^{-\beta(H_S+H_B)}}{Z_SZ_B}UU^\dagger\right] \qquad (2.60)\\ &= \mathrm{Tr}_E\left[\frac{e^{-\beta(H_S+H_B)}}{Z_SZ_B}\right] = \frac{e^{-\beta H_S}}{Z_S} = \gamma_S, \qquad (2.61)\end{aligned}$$

where we use $[U, H_S + H_B] = 0$ to write the Eq. (2.60). □

Proposition 25 (Time-translation invariance)**.** *Let us define the unitary quantum channel on the Hilbert space of the system S representing time translation as $\mathcal{G}_t^S(\,\cdot\,) = e^{-iH_St}(\,\cdot\,)e^{+iH_St}$. The action of thermal operation on the system S commutes with these time translation i.e.,*

$$\mathcal{E}(\mathcal{G}_t^S(\,\cdot\,)) = \mathcal{G}_t^S(\mathcal{E}(\,\cdot\,)) \qquad (2.62)$$

Proof. Similarly as previous proposition 24, we shall use the energy preserving property of the unitary U to prove the claim.

$$\begin{aligned}\mathcal{E}(\mathcal{G}_t^S(\rho)) &= \mathrm{Tr}_E\left[U\Big(e^{-itH_S}\rho e^{itH_S}\otimes\gamma_B\Big)U^\dagger\right] = \mathrm{Tr}_E\left[U\Big(e^{-itH_S}\rho e^{itH_S}\otimes e^{-itH_B}\gamma_B e^{-itH_B}\Big)U^\dagger\right] \\ &= \mathrm{Tr}_E\left[U\Big(e^{-it(H_S+H_B)}(\rho\otimes\gamma_B)e^{it(H_S+H_B)}\Big)U^\dagger\right] \qquad (2.63)\\ &= \mathrm{Tr}_E\left[e^{-it(H_S+H_B)}\Big(U(\rho\otimes\gamma_B)U^\dagger\Big)e^{it(H_S+H_B)}\right] \qquad (2.64)\\ &= e^{-itH_S}\;\mathrm{Tr}_E\Big[U\Big(\rho\otimes\gamma_B\Big)U^\dagger\Big]\;e^{+itH_S} = \mathcal{G}_t^S(\mathcal{E}(\rho)), \qquad (2.65)\end{aligned}$$

where we use $[U, H_S + H_B] = 0$ to write from Eq. (2.63) to Eq. (2.64). □

As a consequence of above mentioned theorem

Proposition 26 (Covariance of dephasing map)**.** *The action of thermal operation $\mathcal{E}$ commutes with the dephasing map $\mathcal{D}$ acting on the state ρ i.e.,*

$$\mathcal{E}(\mathcal{D}(\rho)) = \mathcal{D}(\mathcal{E}(\rho)) \qquad (2.66)$$

where

$$\mathcal{D}(\rho) = \lim_{s\to\infty}\frac{1}{s}\int_0^s e^{-itH_S}\rho e^{+itH_S} \qquad (2.67)$$

Proof. We shall easily see this from the following:

$$\mathcal{E}(\mathcal{D}(\rho)) = \lim_{s\to\infty}\frac{1}{s}\int_0^s \mathcal{E}\left(e^{-itH_S}\rho e^{+itH_S}\right) = \lim_{s\to\infty}\frac{1}{s}\int_0^s e^{-itH_S}\mathcal{E}(\rho)e^{+itH_S} = \mathcal{D}(\mathcal{E}(\rho)), \quad (2.68)$$

where in the last line we use result of theorem 25 to write the second equality. ☐

These properties given in proposition 25 and 26 has some important implications for the action of thermal operations on states. In particular, we proceed to show that it allows us to restrict ourselves to the set of quantum states that do not have coherences in the energy eigenbasis to describe work and heat, which are significantly easier to deal with. The problem of dealing with coherence in this approach to quantum thermodynamics is a very important one, but fewer results exist regarding which transitions between states are possible. We outline some of the most important ones in section 2.5. In any case, most of the work presented here will focus on that subset of states that do not have coherence in the energy eigenbasis.

2.4 Describing the notion of *work*

In this section, we will delve into the concept of work, which is another fundamental aspect of classical thermodynamics, after discussing the thermodynamic ordering between classical states. Initially, we will elucidate the significance of free energy in traditional thermodynamic transitions between equilibrium states. It acts as a limiting factor on the maximum work that can be extracted or invested during the process. Subsequently, we will demonstrate how this idea can be generalized to include general classical states that are not in equilibrium, emphasizing the importance of information in the energetics of such states. We will then introduce the resource-theoretic approach to work extraction, discussing the notions of average, deterministic, and single-shot work extraction protocols. Finally, we will use the findings of this section to argue for the uniqueness of the thermal Gibbs state as the only permissible free state in the resource theory of thermodynamics. It is important to note that the results we present here are limited to classical states. This result has been extended to a quantum scenario where the coherence is present [84]. We shall proceed briefly overviewing the work extraction in equilibrium and non-equilibrium scenarios.

2.4.1 Equilibrium scenario

In this section, we will explain how to determine the amount of work performed on a system that is in contact with a thermal equilibrium bath, while external control parameters such as volume or magnetic field change over a specific period of time. To accomplish this, we will use the notation $\boldsymbol{x} = (q, p)$ to refer to a point in the position-momentum phase space of the system. The system's Hamiltonian is represented by $H(\boldsymbol{x},\alpha)$, where $\alpha \in [0,1]$ represents the path ϕ in the external parameter space. Assuming a constant switching rate, $\frac{d\lambda}{dt} = 1/\tau$, where τ is the total duration of the process, we can determine the work done on the system by measuring the change in energy along the trajectory, starting with the initial state $\boldsymbol{x}_0$, as

$$W_{\boldsymbol{x}_0} := \int_0^\tau dt \frac{d\lambda}{dt}\frac{\partial}{\partial\alpha} H(\boldsymbol{x}(t),\alpha). \tag{2.69}$$

Assuming the system is in thermal equilibrium, we can express the probability density function as:

$$p(\boldsymbol{x},\alpha) = \frac{e^{-\beta H(\boldsymbol{x},\alpha)}}{Z(\alpha)} \quad ;\text{where} \quad Z(\lambda) = \int d\boldsymbol{x} e^{-\beta H(\boldsymbol{x},\lambda)}. \tag{2.70}$$

Using this, we can calculate the average amount of work done on the system initially in equilibrium as:

$$\langle W\rangle = \int_0^1 d\alpha \int d\boldsymbol{x} \frac{e^{-\beta H(\boldsymbol{x},\alpha)}}{Z(\alpha)} \frac{\partial}{\partial\alpha} H(\boldsymbol{x},\alpha), \tag{2.71}$$

which can be rewritten as:

$$\begin{aligned}\langle W\rangle &= \int_0^1 d\alpha \int d\boldsymbol{x} \frac{-\frac{1}{\beta}\frac{d}{d\alpha} e^{-\beta H(\boldsymbol{x},\alpha)}}{Z(\alpha)} = -\frac{1}{\beta}\int_0^1 d\alpha \frac{\frac{d}{d\alpha}\int d\boldsymbol{x} e^{-\beta H(\boldsymbol{x},\alpha)}}{Z(\alpha)} \\ &= -\frac{1}{\beta}\int_0^1 d\alpha \frac{\frac{d}{d\alpha}Z(\alpha)}{Z(\alpha)} = -\frac{1}{\beta}\int_0^1 d\alpha \frac{d}{d\alpha}\log(Z(\alpha)) = -\frac{1}{\beta}(\log\Big(\frac{Z(1)}{Z(0)}\Big).\end{aligned} \tag{2.72}$$

We can define the free energy function as:

$$F(\alpha) = E(\alpha) - \frac{1}{\beta}S(\alpha), \tag{2.73}$$

where $E(\alpha)$ and $S(\alpha)$ denote the average energy and entropy of the system, respectively. The free energy can then be calculated as:

$$\begin{aligned} E(\alpha) &= \int d\boldsymbol{x} \frac{e^{-\beta H(\boldsymbol{x},\alpha)}}{Z(\alpha)} H(\boldsymbol{x},\alpha) = \frac{\frac{\partial}{\partial\beta}\int d\boldsymbol{x} e^{-\beta H(\boldsymbol{x},\alpha)}}{Z(\alpha)} = -\frac{\partial}{\partial\beta}\log Z(\alpha), \\ \frac{1}{\beta}S(\alpha) &= -\frac{1}{\beta}\int d\boldsymbol{x} \frac{e^{-\beta H(\boldsymbol{x},\alpha)}}{Z(\alpha)} \log\Big(\frac{e^{-\beta H(\boldsymbol{x},\alpha)}}{Z(\alpha)}\Big) = E(\alpha) + \frac{1}{\beta}\log(Z(\alpha)). \end{aligned} \tag{2.74}$$

This allows us to obtain the free energy as:

$$F(\alpha) = E(\alpha) - \frac{1}{\beta}S(\alpha) = -\frac{1}{\beta}\log(Z(\alpha)). \tag{2.75}$$

We observe see that in an infinitely slow driving process, the work done on the system is equal to the difference in free energy between the final and initial states. However, for a finite driving speed, the process becomes irreversible. By using Jarzynski's equality $e^{-\beta\Delta F} = \langle e^{-\beta W}\rangle$ from [27] and applying Jensen's inequality, we arrive at the following expression:

$$\langle W \rangle \geq \Delta F. \tag{2.76}$$

This expression essentially restates the second law of thermodynamics. According to this law, when work is done on a system, the minimum amount of work required for the transformation is at least equal to δF, and hence $\langle W \rangle \geq 0$. Conversely, when a system performs work, the maximum amount of work that can be extracted is limited by $|\delta F|$, and $\langle W \rangle \geq 0$. In other words, the change in free energy sets the upper limit on the work that can be extracted from the system.

2.4.2 Non-equilibrium scenario

The concept of free energy $F(\alpha)$ is initially only applied to thermal equilibrium states. However, by examining its operational significance, we can extend its definition to encompass non-equilibrium states as well. In particular, we show that the conventional expression $F(\alpha) = E(\alpha) - \frac{1}{\beta}S(\beta)$, when suitably generalized, measures the maximum average work that can be extracted from an out-of-equilibrium system. Rather than studying classical continuous systems with states represented by points $\boldsymbol{x} = (q, p)$ in phase space, we will connect to the resource-theoretic framework that deals with finite-dimensional systems. Consequently, the state space will become discrete, with states identified by the set $\{j\}$. The Hamiltonian, which is parametrized by an external parameter α, will then take on values $E_i(\alpha)$, while the classical states $\boldsymbol{p}$ will indicate the distribution of energy states. This is precisely equivalent to a quantum system described by the Hamiltonian $H(\alpha) = \sum_i E_i(\alpha)|E_i(\alpha)\rangle\langle E_i(\alpha)|$ when we limit ourselves to states that are diagonal in the energy eigenbasis, with the diagonal elements given by the classical state $\boldsymbol{p}$. The eigenvalues of the Gibbs state is given by the expression

$$\gamma_i(\alpha) = \frac{e^{-\beta E_i(\alpha)}}{Z(\alpha)}, \tag{2.77}$$

where $Z(\alpha)$ is the partition function. The average energy and entropy of the classical state $\boldsymbol{p}$ is given by

$$E(\boldsymbol{p}, \alpha) = \sum_i p_i E_i(\alpha), \quad ; \quad S(\boldsymbol{p}, \alpha) = S(\boldsymbol{p}) = -\sum_i p_i \log p_i. \tag{2.78}$$

Thus, we can extend the notion of free energy to non-equilibrium states as follows:

$$F(\boldsymbol{p}, \alpha) = E(\boldsymbol{p}, \alpha) - \frac{1}{\beta}S(\boldsymbol{p}, \alpha) = \sum_i p_i E_i(\alpha) + \frac{1}{\beta}\sum_i p_i \log p_i = \frac{1}{\beta}D(\boldsymbol{p}\|\gamma(\alpha) - \log(Z(\alpha))), \tag{2.79}$$

where we have an information theoretic notion of relative entropy as

$$D(\boldsymbol{p}\|\boldsymbol{\gamma}(\alpha)) := \sum_i p_i \log\left(\frac{p_i}{\gamma_i(\alpha)}\right) = \sum_i p_i \log p_i + \beta \sum_i p_i E_i(\alpha) + \log(Z(\alpha)). \tag{2.80}$$

In the previous chapter, we observed that $D(\boldsymbol{p}\|\boldsymbol{\gamma}(\alpha))$ is always non-negative, and equality is achieved only if $\gamma(\alpha) = \boldsymbol{p}$. Therefore, the free energy is minimized at the thermal equilibrium state. The current assertion is that the maximum work extractable during a transformation from a system with a Hamiltonian $H(0)$ and in a classical state $\boldsymbol{p}$ to a system described by the final Hamiltonian $H(1)$ and a classical state $\boldsymbol{q}$, is given by

$$\langle W\rangle = F(\boldsymbol{p}, 0) - F(\boldsymbol{q}, 1). \tag{2.81}$$

Assuming that the initial and final Hamiltonians are the same, representing a cyclic process, we aim to maximize the extracted work while reaching a thermal final state that minimizes free energy. This objective leads to the following equality:

$$\langle W\rangle(\boldsymbol{p}) = \Delta F(\boldsymbol{p}) := F(\boldsymbol{p}, 0) - F(\boldsymbol{\gamma}, 0) = \frac{1}{\beta} S(\boldsymbol{p}|\boldsymbol{\gamma}). \tag{2.82}$$

To illustrate how this can be achieved, we present examples for a qubit in box 2.1. This protocol will be employed to explain work extraction in the resource-theoretic framework in the next section.

In the example discussed in box 2.1, it was observed that even the ground state of a system possesses energy when a heat bath is present, indicating that information about the system state carries energy. This observation was first made by Szilard [85, 86], who developed an engine that converts information about the occupied degenerate state (i.e., 1 bit) into $\frac{\log 2}{\beta}$ work. The relationship between thermodynamics and information becomes even more apparent in Eq. (2.82), where the amount of work extracted is proportional to the relative entropy, which quantifies the information lost when the thermal distribution γ is used to estimate the system state $\boldsymbol{p}$.

The qubit result shown in box 2.1 can be generalized to systems of any dimension d. In [87], it was demonstrated that by performing a sequence of level transformations (while the system remains isolated from the heat bath) and complete thermalization, we can extract work that approaches the free energy difference. Suppose we have an initial Hamiltonian $H(0)$, its corresponding thermal Gibbs state $\gamma(0)$, and an initial system state $\boldsymbol{p}$. To extract work, we follow these steps. First, we modify the Hamiltonian to $H(1)$ such that the new thermal state $\gamma(1)$ matches the initial state $\boldsymbol{p}$. Then, we connect the system to the heat bath and gradually change the Hamiltonian back to $H(0)$. By the end of the process, the system will be in the thermal state of the original Hamiltonian, and we will extract $\frac{1}{\beta} D(\boldsymbol{p}\|\boldsymbol{\gamma}(0))$ work. Note that these are the same steps outlined in the qubit example of box 2.1, with the

Box 2.1: **Work extraction from incoherent qubit state**

Let's consider a qubit system initially described by a Hamiltonian $H(0, E) = E|1\rangle\langle 1|$ and prepared in the excited state $|E\rangle\langle E|$, which can be represented by a classical state $\boldsymbol{p} = (0\ 1)^T$. The maximum change in free energy can be obtained through the following equation:

$$\Delta F(\boldsymbol{p}) = E + \frac{1}{\beta}\log Z. \tag{2.83}$$

To extract the amount of work given by the above expression, a specific protocol can be implemented which is outlined below.

1. *Quench:* Firstly, the initial step involves a rapid transformation of the Hamiltonian H to $H(0, 0)$, either at any speed or by isolating the system from the thermal bath. The resulting Hamiltonian has the same eigenstates as H but with degenerate eigenvalues equal to zero. The system's state remains represented by $\boldsymbol{p}$, but its energy decreases by E. This process corresponds to the energetic aspect of the extracted work.
2. *Relaxation:* The second step entails altering the Hamiltonian to $H(\infty, 0)$ while the system remains isolated from the thermal bath, with ∞ denoting an eigenvalue much greater than $\frac{1}{\beta}$. Since only the energy of an unoccupied level is modified without any impact on the distribution, the system's energy remains constant. Subsequently, the system is gradually connected to the thermal bath, and the Hamiltonian is slowly changed from $E = \infty$ to E. This results in the following amount of extracted work:

$$-\int_{\infty}^{E} \gamma_0(E, 0)dE = \int_{E}^{\infty} \frac{e^{-\beta E}}{1 + e^{-\beta E}}dE = \frac{1}{\beta}\log Z(0, E), \tag{2.84}$$

   which represents the information part of the extracted work.

exception of a constant shift in the energy spectrum.

2.4.3 Resource theoretic analysis of work extraction

Up to this point, we have highlighted the significance of generalised free energy as a metric to gauge the maximum feasible work that can be drawn from a system. The work extraction methods described thus far rely on controlling and altering the external parameters that specify the system's Hamiltonian. However, in a resource theoretic approach to thermodynamics, we try to avoid the use of external systems in order to prevent the bringing free resources and explicitly model everything. Hence, it is unclear whether one can obtain the amount of work equivalent to the system's free energy variation within a resource theory framework. In this regard, we will provide a brief explanation of how this can be accomplished for average work extraction and introduce the concepts of deterministic and single-shot work extractions.

The work in resource theoretic approach differs from the previous section by incorporating a work storage device or *battery* as an integral part of the system, along with a *clock* capable of simulating effectively the time-dependent nature of the system's Hamiltonian. As a result, the Hamiltonian governing the entire system becomes time-dependent. The system now comprises three components: the work storage system denoted as W, the clock designated as C, and the system under consideration represented as S, and follows a Gibbs-preserving map of the collective Hamiltonian SCW.

We denote the Gibbs state of system S is denoted by $\boldsymbol{\gamma}_S$, where $\gamma_{S,i}$ is given as $\frac{e^{-\beta E_i^S}}{Z_S}$. Here, $\{E_i\}_{i=1}^d$ represents the spectrum of the Hamiltonian of system S, and Z_S denotes the partition function. We consider the Hamiltonian of the work storage W as a qubit, (also referred as the *wit*), with an energy gap of w, which can be expressed as $H_W = w|1\rangle\langle 1|$. We write the Gibbs state of W as $\boldsymbol{r}^{\text{Gibbs}}$ such that

$$\boldsymbol{r}^{\text{Gibbs}} = \frac{1}{1+e^{-\beta w}} \begin{pmatrix} 1 \\ e^{-\beta w} \end{pmatrix} := \begin{pmatrix} r_0 \\ r_W \end{pmatrix}. \tag{2.85}$$

The concept of deterministic work extraction describes where the initial and final energies of battery are restricted to either 0 or w. Furthermore, the energy alteration of battery is always either equal to w or $-w$, with a probability one, depending on the specific context being studied.

2.4.3.1 Work of formation

Let us begin by examining the minimum work necessary to generate a non-equilibrium classical state $\boldsymbol{p}$ from the equilibrium classical state $\boldsymbol{\gamma}_S$, under the assumption that the initial and final Hamiltonians of the system are the same. Hence, there is no need to explicitly include the clock C in the framework. Moreover, we suppose that w is a positive quantity.

The initial classical state of the system S and work storage W are $\boldsymbol{\gamma}_S$ and $\boldsymbol{r}^{\text{up}} := (0,1)^T$, respectively. The final classical state of the system S and work storage is $\boldsymbol{p}$ and $\boldsymbol{r}^{\text{down}}$. The Fig. 2.1 shows the relative Lorenz curves of initial and final classical state of the combined system SW, alongwith the the relevant ∞ - divergences. From the fig. 2.1, we see that state conversion is possible, if and only if

$$e^{D_\infty(\gamma_S \otimes \boldsymbol{r}^{\text{up}} \| \gamma_S \otimes \boldsymbol{r}^{\text{Gibbs}})} \leq e^{D_\infty(\boldsymbol{p} \otimes \boldsymbol{r}^{\text{down}} \| \gamma_S \otimes \boldsymbol{r}^{\text{Gibbs}})}. \tag{2.86}$$

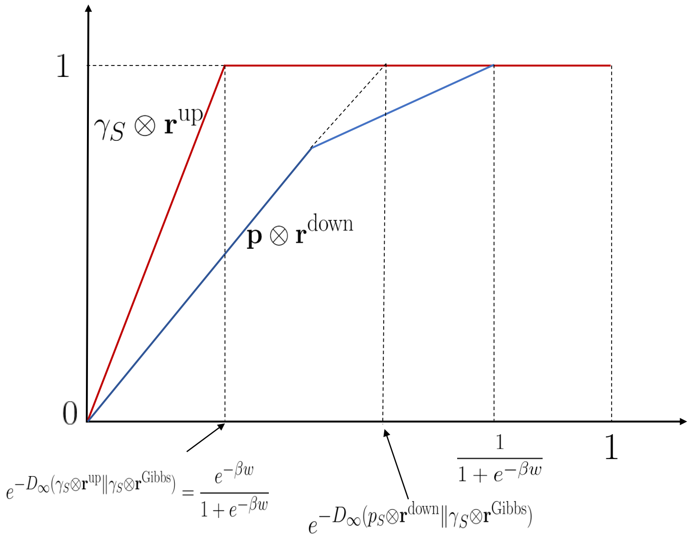


Figure 2.1: The relative Lorenz curves depict the transformation of system S's Gibbs state, γ_S, to a non-equilibrium state, $\boldsymbol{p}$, at a cost of $w > 0$. This conversion is feasible only if $\gamma_S \otimes \boldsymbol{r}^{\mathrm{up}}$ thermo-majorizes $\boldsymbol{p} \otimes \boldsymbol{r}^{\mathrm{down}}$. It is essential to note that the shape of the Lorenz curve for $\boldsymbol{p} \otimes \boldsymbol{r}^{\mathrm{down}}$ has been intentionally selected to be simplistic, rather than generic.

This Eq. (2.86) further reduces to

$$\frac{e^{-\beta w}}{1+e^{-\beta w}} \geq \frac{e^{-\beta w}}{1+e^{-\beta w}} e^{-D_\infty(\boldsymbol{p} \| \gamma_S)}. \tag{2.87}$$

Thus, we obtain the necessary and sufficient condition for the state conversion as

$$w \geq \frac{1}{\beta} D_\infty(\boldsymbol{p} \| \gamma_S), \tag{2.88}$$

that gives the lower bound of the necessary work.

2.4.3.2 Work extraction

Let us now consider how much work can be maximally extracted from the initial classical state $\boldsymbol{p}$ of S, assuming that the initial and final Hamiltonians of S remain the same, which means that the clock C does not need to be explicitly considered. Let us assume that the value of w is negative.

The initial state of work storage W is $\boldsymbol{r}^{\mathrm{down}} = (1, 0)^T$, while the final classical state of S is γ_S and that of W is $\boldsymbol{r}^{\mathrm{up}} = (0, 1)^T$, so the final distribution of SW is $\gamma_S \otimes \boldsymbol{r}^{\mathrm{up}}$. In this setting, $-w > 0$ represents the work that is extracted from system S and finally stored in work storage W.

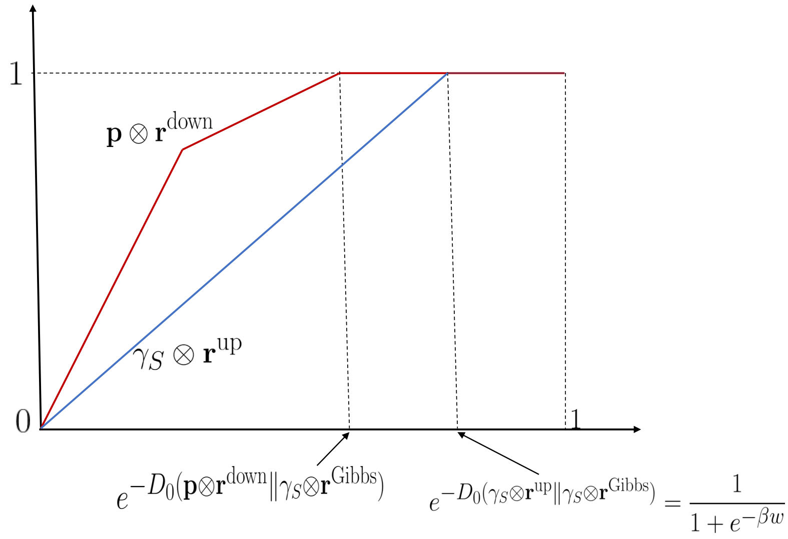


Figure 2.2: The relative Lorenz curves depict the transformation of an arbitrary initial state $\boldsymbol{p}$ of system S into the Gibbs state $\boldsymbol{\gamma}_S$ via a work extraction of $-w > 0$. For this conversion to occur, it is necessary and sufficient that $\boldsymbol{p} \otimes \boldsymbol{r}^{\text{down}}$ thermo-majorizes $\boldsymbol{\gamma}_S \otimes \boldsymbol{r}^{\text{up}}$. Note that the Lorenz curve for $\boldsymbol{p} \otimes \boldsymbol{r}^{\text{down}}$ is chosen to be simple, rather than general.

The Lorenz curves of the initial and final classical states of system and work storage SW are presented in Fig. 2.2, along with their 0-divergences. The state conversion is feasible only if the following inequality holds:

$$e^{-D_0(\boldsymbol{p}\otimes\boldsymbol{r}^{\text{down}}\|\boldsymbol{\gamma}_S\otimes\boldsymbol{r}^{\text{Gibbs}})} \leq e^{-D_0(\boldsymbol{\gamma}_S\otimes\boldsymbol{r}^{\text{up}}\|\boldsymbol{\gamma}_S\otimes\boldsymbol{r}^{\text{Gibbs}})}, \tag{2.89}$$

which can be simplified to

$$\frac{e^{-\beta w}}{1+e^{-\beta w}} e^{-D_0(\boldsymbol{p}\|\boldsymbol{\gamma}_S)} \leq \frac{1}{1+e^{-\beta w}}. \tag{2.90}$$

Thus, we can obtain the necessary and sufficient condition for the state conversion:

$$-w \leq \frac{1}{\beta} D_0(\boldsymbol{p}\|\boldsymbol{\gamma}_S), \tag{2.91}$$

which sets an upper limit on the extracted work $-w$.

The protocol proposed in Ref. [87] described in box 2.1 achieves the equality in Eq. (2.91). The work storage W and clock C are not explicitly taken into account. The protocol consists of two steps:

1. *Quench:* In the first step, the energy level of i is raised to infinity while keeping all

other energy levels constant. This process, called a *quench*, instantly increases the energy level i with population $p_i = 0$, and hence no work is performed on system S.

2. *Relaxation:* Once we have allowed for the relaxation of system S, we proceed to gradually restore the previously raised energy level back to its original values through a quasi-static process.

The amount of work that can be extracted during a quasi-static process is equal to the change in the system's equilibrium free energies, which is given by

$$-w = -\frac{1}{\beta}\log\left(\frac{Z_0}{Z}\right) = -\frac{1}{\beta}\log\Big(\sum_{i:p_i>0}\gamma_{S,i}\Big) = \frac{1}{\beta}D_0(\boldsymbol{p}\|\boldsymbol{\gamma}_S), \tag{2.92}$$

where $Z_0 := \sum_{i:p_i>0} e^{-\beta E_i}$. The work does not fluctuate in the entire process, making it a single-shot protocol.

2.4.3.3 Equilibrium transition

Finally, Let us consider the transitions between the Gibbs state of system S by modifying its Hamiltonian from an initial state to a final state with the aid of the clock C. Through this specific configuration, we can reproduce the conventional expression of the second law as denoted by Eq. (2.76), which is identified by the equilibrium free energies of the system.

We make the assumption that the energy levels E_i describe the Hamiltonian of system S when the clock displays "0" and $\tilde{E}_i$ when it displays "1". The Gibbs states of the initial and final Hamiltonians correspond to the initial and final classical states of S, which are represented by $\boldsymbol{p}$ and $\tilde{\boldsymbol{p}}$, respectively. These Gibbs states are defined as $p_i = \frac{1}{Z}e^{-\beta E_i}$ and $\tilde{p}_i = \frac{1}{\tilde{Z}}e^{-\beta\tilde{E}_i}$, where Z and $\tilde{Z}$ are the partition functions. To simplify the notation, we will omit the superscript "Gibbs" from $\boldsymbol{p}$ and $\tilde{\boldsymbol{p}}$. The free energies associated with these Gibbs states are expressed as $F := -\beta^{-1}\log Z$ and $\tilde{F} := -\frac{1}{\beta}\log\tilde{Z}$.

To simplify our analysis, we assume that clock C has only two possible states, namely "0" and "1". The classical state of C is represented by the vector $(c_0, c_1)^T$ in general. In this case, we consider the classical state of C to be $\boldsymbol{c} = (1,0)^T$, while the final state is denoted by $\tilde{\boldsymbol{c}} = (0,1)^T$. By noting that clock C is coupled to S such that clock C induces the change of the Hamiltonian of H_S, the total Gibbs state of system and clock SC should be given by

$$\boldsymbol{p}_{SC}^{\text{Gibbs}} = \frac{Z}{Z+\tilde{Z}}\boldsymbol{p}\otimes\boldsymbol{c} + \frac{\tilde{Z}}{Z+\tilde{Z}}\tilde{\boldsymbol{p}}\otimes\tilde{\boldsymbol{c}}. \tag{2.93}$$

Suppose that the initial and final states of W are respectively given by

$$\boldsymbol{r}^{\text{down}} := (0,1)^T \quad ; \quad \boldsymbol{r}^{\text{up}} := (0,1)^T. \tag{2.94}$$

Here, we supposed that $w > 0$ (i.e., the case of work extraction), while this is not actually

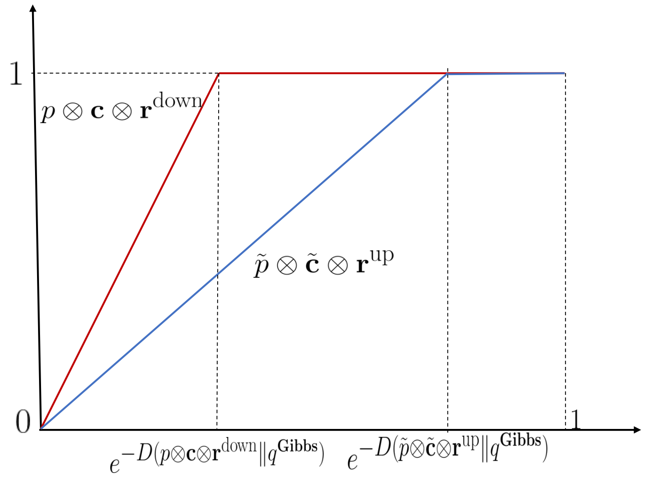


Figure 2.3: This figure illustrates relative Lorenz curves for a transition between Gibbs state of S. The state conversion is possible, if and only if $\boldsymbol{p}\otimes\boldsymbol{c}\otimes\boldsymbol{r}^{\text{down}}$ thermomajorizes $\tilde{\boldsymbol{p}}\otimes\tilde{\boldsymbol{c}}\otimes\boldsymbol{r}^{\text{up}}$

necessary for the following argument.

The Gibbs state of the combined system, which includes the clock and weight, denoted as SCW, can be expressed as $\boldsymbol{p}_{SC}^{\text{Gibbs}}\otimes\boldsymbol{r}^{\text{Gibbs}}$. The entire SCW system undergoes a transformation through a map that maintains the total Gibbs state $\boldsymbol{q}^{\text{Gibbs}}:=\boldsymbol{p}_{SC}^{\text{Gibbs}}\otimes\boldsymbol{r}^{\text{Gibbs}}$. In this situation, the initial and final Lorenz curves are comprised of a straight and horizontal line, as shown in Fig. 2.3. Hence, $D_\alpha(\boldsymbol{p}\otimes\boldsymbol{c}\otimes\boldsymbol{r}^{\text{down}}\|\boldsymbol{p}_{SC}^{\text{Gibbs}}\otimes\boldsymbol{r}^{\text{Gibbs}})$ reduces to a single value for all $0\leq\alpha\leq\infty$. Specifically, when $\alpha=1$, the KL divergence is equivalent to all other Renyi divergences with different values of α. Therefore, from the Lorenz curves depicted in Fig. 2.3, the conversion of states is feasible if and only if

$$e^{-D(\boldsymbol{p}\otimes\boldsymbol{c}\otimes\boldsymbol{r}^{\text{down}}\|\boldsymbol{p}_{SC}^{\text{Gibbs}}\otimes\boldsymbol{r}^{\text{Gibbs}})}\leq e^{-D(\tilde{\boldsymbol{p}}\otimes\tilde{\boldsymbol{c}}\otimes\boldsymbol{r}^{\text{up}}\|\boldsymbol{p}_{SC}^{\text{Gibbs}}\otimes\boldsymbol{r}^{\text{Gibbs}})}. \tag{2.95}$$

Furthermore, we can write

$$e^{-D(\boldsymbol{p}\otimes\boldsymbol{c}\otimes\boldsymbol{r}^{\text{down}}\|\boldsymbol{p}_{SC}^{\text{Gibbs}}\otimes\boldsymbol{r}^{\text{Gibbs}})} = \frac{Z}{(Z+\tilde{Z})}\times\frac{e^{-\beta w}}{1+e^{-\beta w}} \tag{2.96}$$

$$e^{-D(\tilde{\boldsymbol{p}}\otimes\tilde{\boldsymbol{c}}\otimes\boldsymbol{r}^{\text{up}}\|\boldsymbol{p}_{SC}^{\text{Gibbs}}\otimes\boldsymbol{r}^{\text{Gibbs}})} = \frac{\tilde{Z}}{(Z+\tilde{Z})}\times\frac{1}{1+e^{-\beta w}} \tag{2.97}$$

Thus, we conclude that the necessary and sufficient conditions for the state conversion as

$$-w\leq-(F-\tilde{F}) \tag{2.98}$$

which is nothing but the second law given in Eq. (2.76). The result presented in Eq. (2.98) agrees with the fact that work fluctuation becomes negligible in the quasistatic limit, which indicates that equilibrium transitions can be achieved through single-shot protocols.

2.5 Evolution of coherence under thermal operation

In this chapter and throughout most of this thesis, we examine a specific set of states ρ_S that have a block diagonal form in the local energy eigenbasis, meaning that $[\rho_S, H_S] = 0$. We defined the as energy incoherent states (see definition 24). However, a pertinent question arises if states possess coherence in the energy eigenbasis between non-degenerate energy levels. This is a complex question with an unknown general solution, but progress has been made by considering energy coherence in the framework of resource theory, specifically the theory of asymmetry [62, 88]. One approach is to view states with energy coherence as violating a symmetry associated with the time translation operation described in theorem 25. In other words, such states do not remain invariant under the action of time translations.

By adopting the resource theory framework, specifically the theory of asymmetry, one can identify states that abide by the symmetry associated with time translation, indicating that they remain unaltered when subjected to time translations. However, determining the fate of states that exhibit coherence between non-degenerate energy levels remains a thorny issue without a general solution. Nonetheless, progress has been made in this area, leading to the establishment of supplementary restrictions that pairs of states with coherence must fulfil to allow for a transition. These limitations are briefly discussed in several works [83, 89, 90].

- One way to measure the deviation of a quantum state from its dephased version is to compute a distance between them. A basic example of this is the relative entropy between an arbitrary quantum state ρ and its dephased version $\mathcal{D}(\rho)$.

  $$D(\rho\|\mathcal{D}(\rho)) = \mathrm{Tr}(\rho\log\rho) - \mathrm{Tr}(\rho\log(\mathcal{D}(\rho))), \tag{2.99}$$

  which can only decrease as due to the data processing inequality of the relative entropy under quantum maps i.e., given a thermal operation $\mathcal{E}$, we have

  $$D(\rho\|\mathcal{D}(\rho)) \geq D(\mathcal{E}(\rho)\|\mathcal{E}(\mathcal{D}(\rho))) = D(\sigma\|\mathcal{D}(\sigma)). \tag{2.100}$$

  Similar monotones can be defined via other Renyi divergences.

- Using the properties of time-translation invariance (see theorem 25) and Gibbs state preservation, we can derive a bound on the magnitude of coherent terms in a quantum state ρ, represented by ρ_{ij} when $E_i \neq E_j$. The proof of this bound is beyond the scope of this section, but we present it here for completeness. Suppose $\mathcal{E}(\rho) = \sigma$, and we write $\rho = \sum_{i,j} \rho_{ij} |E_i\rangle\langle E_j|$. Then, we have:

$$|\sigma_{kl}| \geq \sum_{i,j,E_i<E_k} |\rho_{ij}| e^{-\beta(E_k - E_i)} + \sum_{i,j,E_i>E_k} |\rho_{ij}|, \tag{2.101}$$

where the sum is over pairs of i, j such that $E_i - E_j = E_k - E_l$. It is worth noting that while the issue of coherence is thermodynamically important, it may not be as significant in the context of work extraction. In fact, it is known that work cannot be extracted from coherence unless a reference frame is available, and even then, the optimal method for extracting work from coherence is unclear.

Chapter 3

Fluctuation dissipation-like relation in thermodynamic distillation processes

3.1 Introduction

Thermodynamics has greatly influenced the natural sciences and has played a crucial role in the development of a wide range of technologies, including cooling systems and spaceships. The theory, which explains the behaviour of macroscopic systems in equilibrium, offers a comprehensive comprehension of state transformations allowed by a few macroscopic quantities like entropy and work [91, 92]. Nevertheless, the macroscopic depiction of thermodynamics is limited to average quantities, overlooking the increasingly significant fluctuations of these quantities in smaller systems [31, 93]. To address this limitation, researchers have focused on fluctuations around these averages and their impact on system dynamics. This line of inquiry dates back to Einstein and Smołuchowski and has resulted in the well-established concept of the fluctuation-dissipation theorem [94, 95, 96, 97]. This theorem, validated by experimental evidence, describes a system's response to an external perturbation in terms of its fluctuation properties in thermal equilibrium [98, 99].

In contrast to the thermodynamic approach, an alternative approach on comprehending the behaviour of smaller systems is founded on resource theories [34, 70, 100, 101]. This viewpoint endeavours to expand statistical mechanics beyond the bounds of the thermodynamic limit and equilibrium assumptions by taking into account scenarios involving substantial fluctuations, termed single-shot statistical mechanics [102, 103]. The question that arises is whether fluctuation-dissipation relations exist in this resource-theoretic framework. Although efforts have been made to establish a connection between information-theoretic and fluctuation theorem approaches [104, 105], no explicit association with dissipation has been established as yet. Recently, methodologies have been devised to analyze free energy dissipation within a resource-theoretic framework by studying the irreversibility of thermodynamic processes due to finite-size effects [63, 106, 107, 108]. However, these results were limited to the quasi-classical scenario of energy-incoherent states and did not account for quantum effects that arise in even smaller systems, where fluctuations around thermodynamic averages are no longer purely thermal in origin.

Our work advances towards a quantum framework that characterizes optimal thermodynamic state transformations and establishes a connection between fluctuations and free energy dissipation. We focus on a particular type of the state interconversion processes known as thermodynamic distillations, where a given initial quantum system is transformed, with some error, into a pure energy eigenstate of the final system. Our investigation centres on initial systems that consist of a large number of non-interacting subsystems that are either energy-incoherent and non-identical or pure and identical. Our findings consist of two theorems that form the core of our research. The first theorem presents the optimal transformation error as a function of the free energy difference between the initial and target states, as well as the free energy fluctuations in the initial state. This theorem extends previously derived results on optimal thermodynamic state transformations. The second theorem provides a precise relationship between the free energy fluctuations of the initial state and the minimal amount of free energy dissipated in the optimal thermodynamic distillation process. This conceptually novel theorem does not extend any previously known results and represents our main contribution. It should be noted that the second theorem builds on the first one as one of its fundamental components.

Our research has enabled a rigorous examination of crucial thermodynamic processes. Firstly, we have extended the analysis of work extraction to cover non-identical incoherent states, as well as pure states. Using our main results, we have derived a second-order asymptotic expression for the optimal transformation error while extracting a specific amount of work from the initial system. Additionally, we have verified the accuracy of this expression by comparing it with the numerically optimized work extraction process. Secondly, we have explored the optimal energetic cost of erasing N independent bits prepared in arbitrary states. In this instance, we have calculated the optimal transformation error for the erasure process as a function of invested work. Thirdly, we have studied the optimal thermodynamically-free communication scheme, which involves encoding information into a quantum system without using any extra thermodynamic resources. Our theorems have provided us with the optimal number of messages that can be encoded into a quantum system in a thermodynamically free-way, and we have shown that this result is directly related to the non-equilibrium free energy of the system. We have also demonstrated that this finding can be interpreted as the inverse of the Szilard engine. Our results also establish a link between the fluctuations of free energy and the optimal average decoding error. Finally, we have developed new tools for analyzing approximate transformations and corresponding asymptotic interconversion rates. We have extended previous distillation re-

Box 3.1: **Optimal transformation error for thermodynamic distillation processes**

The optimal thermodynamic process that aims to transform many independent non-equilibrium systems into systems without fluctuations of free energy is characterized by the transformation error ϵ. One of the main results of this chapter aims to show that the value of ϵ can be determined by the following equation:

$$\epsilon = \Phi\left(-\frac{\Delta F}{\sigma(F)}\right), \tag{3.1}$$

where ΔF represents the free energy difference between the initial and target state, $\sigma(F)$ represents the free energy fluctuation in the initial state, and Φ denotes the cumulative normal distribution function which is defined as

$$\Phi(x) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{x} e^{\frac{-t^2}{2}} dt. \tag{3.2}$$

These results have been proven for many independent systems that are in arbitrary incoherent states, as well as for many independent and identical systems in the same pure state. We conjecture this result holds true for many independent systems present in arbitrary mixed states.

sults to include non-identical systems and genuinely quantum states in a superposition of different energy eigenstates.

This Chapter structured as follows. We begin by providing a high-level overview in section 3.2 that provides insight into our research and conveys the underlying physical intuition to a broad audience without the need for delving into technical details. Following this, in section 3.3, we review the resource-theoretic approach to thermodynamics and introduce relevant concepts for applications. Our primary results, which include the optimal transformation error and the fluctuation-dissipation relation for both incoherent and pure states, are presented in the section 3.4. We discuss the thermodynamic interpretation of these results and apply them to three thermodynamic protocols: work extraction, information erasure, and thermodynamically-free communication. The technical derivation of our main findings is detailed in the section 3.5. Finally, in section 3.6, we offer a conclusion and provide a glimpse of future research directions. In this way, we establish a general fluctuation-dissipation relation for thermodynamic distillation processes

Box 3.2: **Fluctuation-dissipation relation for thermodynamic distillation processes**

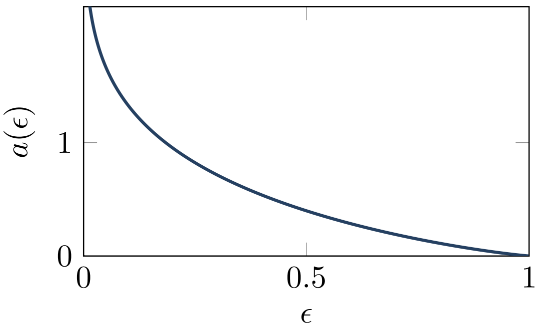
The dissipated free energy in the optimal thermodynamic process of ϵ-approximate transformation from multiple independent non-equilibrium systems into systems with no free energy fluctuations is given by the equation:

$$F_{\text{diss}} = a(\epsilon)\sigma(F), \tag{3.3}$$

where $\sigma(F)$ represents the free energy fluctuation in the initial state. The value of $a(\epsilon)$, which is defined by the equation:

$$a(\epsilon) = -\Phi^{-1}(\epsilon)(1-\epsilon) + \frac{\exp\left(\frac{-(\Phi^{-1}(\epsilon))^2}{2}\right)}{\sqrt{2\pi}}, \tag{3.4}$$

can be used to determine the dissipated free energy. Here, $\Phi^{-1}(x)$ denotes the inverse of the Gaussian cumulative distribution function.



This claim has been proved for many independent systems in identical incoherent states, while it has been demonstrated for many independent systems in identical pure states that the right-hand side of Eq. (3.3) is a lower bound on the value of the function F_{diss}. We conjecture that many independent systems in arbitrary mixed states exhibit the equality in Eq. (3.3).

3.2 High-level description

To provide readers with an initial understanding of our investigation, we present a high-level description of our work before formally outlining the setting in this paper. We seek to identify the fluctuation-dissipation phenomenon in the context of the resource-theoretic approach to thermodynamics. This phenomenon was originally described by Einstein and Smołuchowski and posits that to achieve any ordered motion in a system subjected to random forces, energy proportional to the fluctuations of energy induced by these forces must be dissipated. In contrast, the resource theory of thermodynamics centers around the question of whether one state can be transformed into another state in a thermodynamic manner. Within our framework, we examine the effect of fluctuations present in the initial state of the system on the minimum amount of dissipation required during the state transformation process. We will demonstrate that the appropriate fluctuating and dissipated quantity in the thermodynamic context is the free energy of the system, as we shall see by the end of the section.

To begin, we present a simple example as a warm-up, where our objective is to extract work from a given system. This example can be considered a state transformation, particularly if we explicitly incorporate an ancillary weight system. We consider a model system with a continuous, non-degenerate energy spectrum, where the ground state of energy $E_0 = 0$ is prepared as a probabilistic mixture ρ of different energy eigenstates $|E\rangle$ corresponding to energy E. Mathematically, this can be expressed as

$$\rho = \int_0^\infty p(E)|E\rangle\langle E|dE, \tag{3.5}$$

where $p(E)$ is a probability density function that describes the distribution of the system over its energy levels. Our goal is to utilize this model system, which possesses fluctuating amounts of energy, to produce an almost deterministic change in the energy of another system. In other words, we aim to perform ϵ-deterministic work W, meaning that we seek to change the state of an ancillary weight system from one energy eigenstate $|W_0\rangle$ to another energy eigenstate $|W_0 + W\rangle$ with a probability of $1 - \epsilon$.

How can we accomplish this task? If the probability density function $p(E)$ of the energy eigenstates is zero in the interval $[0, W]$, we can connect the two systems and transfer exactly W units of energy between them. This can be done by shifting the entire energy distribution $p(E)$ down by W while shifting the ancillary weight system up by W, as illustrated in the top panel of Fig. 3.1. However, if most of the probability density function is concentrated far from the ground energy state 0, we need to perform a similar protocol, but we will fail with a probability of

$$\epsilon = \int_0^W p(E), dE, \tag{3.6}$$

since the energy eigenstates with $E \in [0, W]$ cannot be lowered by W, as that would require them to fall below the ground state. Let us use an example to provide further clarity. Consider a Gaussian distribution $p(E)$ with a mean $\langle E\rangle$ and standard deviation σ:

$$p(E) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{1}{2}\frac{(E - \langle E\rangle)^2}{\sigma^2}\right). \tag{3.7}$$

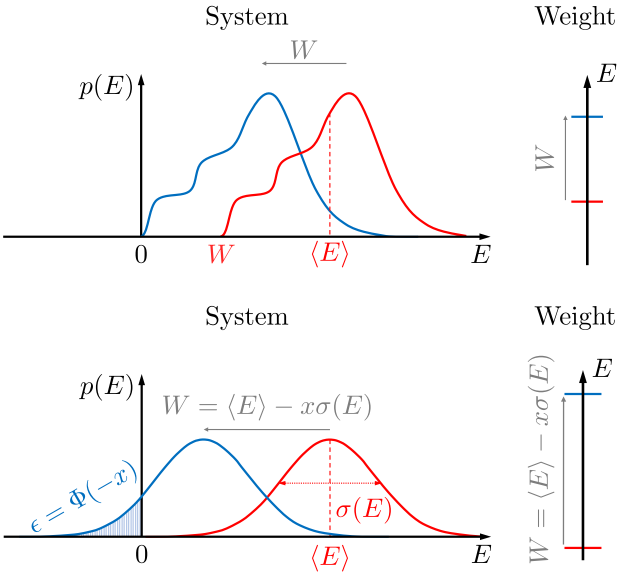


Figure 3.1: **Transforming "fluctuating" to "deterministic" energy.** *Top:* Despite fluctuations in energy, it is unlikely to draw a significant amount of work from the lowest occupied state, as it is far from the ground state. The amount of work that can be drawn, denoted by W, is deterministic, but much smaller than the system's average energy content $\langle E\rangle$. However, it is possible to extract a deterministic amount of work approaching the average energy $\langle E\rangle$ while accepting a probability of failure ϵ. The loss incurred during this process is proportional to the energy fluctuations $\sigma(E)$, and the proportionality constant is determined by ϵ. This extraction process assumes an initial Gaussian distribution with an average energy of $\langle E\rangle$ and a standard deviation of $\sigma(E)$.

This example is particularly relevant to thermodynamics since we are interested in the total energy distributions of a large number of particles, and the central limit theorem states that these distributions can be approximated well by Gaussian distributions. Although the Gaussian distribution is non-zero for energies below the ground state energy 0, we can ignore this as long as the average energy $\langle E\rangle$ is far from zero. In the bottom panel of Fig. 3.1, we demonstrate how shifting down a Gaussian distribution by its mean $\langle E\rangle$ decreased by a multiple of standard deviations $x\sigma$ leads to an error $\epsilon = \Phi(x)$, where Φ is the cumulative normal distribution function as given in Eq. (3.2). This shows that in order to extract work with a fixed success probability, we must dissipate some of the fluctuating energy due to fluctuations. In other words, we must lose some of the fluctuating energy to transform it into (almost) deterministic energy. This simple example gives us an intuition for why fluctuations might be related with dissipation.

The above toy example is limited in its scope and doesn't capture many important aspects of realistic scenarios. For instance, in thermodynamics, we have access not only to mechanical work but also to a thermal bath that can be utilized to draw even more thermodynamic work. Moreover, when dealing with systems of multiple particles, we don't have a non-degenerate spectrum but rather a corresponding density of states for each energy.

Thus, simply shifting the distribution down may not be feasible as there may be fewer low-energy states than high-energy states. Additionally, the example only covers the protocol of work extraction, which is a specific type of general thermodynamic state transformation. Finally, since we're dealing with quantum mechanics, we may encounter coherent superpositions of states within each degenerate energy subspace that can constructively or destructively interfere. As a result, the situation becomes even more complicated and necessitates a formalism that can account for both coherent and incoherent contributions to fluctuations.

Despite the aforementioned complexities, we show in our work that the original insight gained from the simple toy example can be extended to general quantum thermodynamic scenarios with all the features outlined above. The key modification required is the replacement of the concept of average energy and its fluctuations, relevant to mechanical systems, with the concept of average free energy and its fluctuations, relevant to thermodynamic scenarios. In order to account for quantum systems prepared in arbitrary non-equilibrium states, we use the non-equilibrium quantum generalization of the classical expression for free energy, which allows us to define free energy fluctuations rigorously. With these modifications in place, we show that one can apply the intuition described above to investigate general thermodynamic distillation processes. These processes transform generic states with fluctuations of free energy into states with no free energy fluctuations, that is equivalent of *ordered energy* states in the toy example. Specifically, we prove that during such a process, for a fixed success probability of transformation $(1-\epsilon)$, the amount of free energy dissipated is proportional to the initial free energy fluctuations, with the proportionality constant provided in Eq. (3.4).

3.3 Setting the scene

3.3.1 Thermodynamic distillation processes

In order to formally define the thermodynamic distillation process, we begin with recapitulating the set of thermodynamically-free states and transformations that we have introduced in chapter 2. We defined a state of the system that is in equilibrium with a thermal environment E at inverse temperature β is a free state. Therefore, for a system described by a Hamiltonian H, the only free state is given by the thermal Gibbs state

$$\gamma = \frac{e^{-\beta H}}{Z}, \qquad Z = \mathrm{Tr}\left(e^{-\beta H}\right). \tag{3.8}$$

We have introduced the set of free transformations as *thermal operations* (See definition 22 of chapter 2) [33, 34, 70], that act on the system as

$$\mathcal{E}(\rho) = \mathrm{Tr}_E\left(U\left(\rho\otimes\gamma_E\right)U^\dagger\right), \tag{3.9}$$

where U is a joint unitary acting on the system and the thermal environment E that is described by a Hamiltonian H_E and is prepared in a thermal Gibbs state γ_E at inverse temperature β. Moreover, U is commuting with the total Hamiltonian of the system and bath, $[U, H\otimes\mathbb{1}_E + \mathbb{1}\otimes H_E] = 0$. Now we shall define thermodynamic distillation.

Definition 26 (Thermodynamic distillation)**.** A *thermodynamic distillation* process is a thermal operation from a general *initial system* described by a Hamiltonian H and prepared in a state ρ, to a *target system* described by a Hamiltonian $\tilde{H}$ and in a state $\tilde{\rho}$ that is an eigenstate of $\tilde{H}$.

Definition 27 (ϵ- approximate thermodynamic distillation process)**.** An *ϵ-approximate thermodynamic distillation* process from (ρ, H) to $(\tilde{\rho}, \tilde{H})$ is a thermal operation that transforms the initial system (ρ, H) to the *final system* $(\rho_{\text{fin}}, \tilde{H})$ with ρ_{fin} being ϵ away from $\tilde{\rho}$ in the infidelity distance i.e., $\delta(\tilde{\rho}, \rho_{\text{fin}})$ where

$$\delta(\rho_1,\rho_2) := 1 - \left(\mathrm{Tr}\sqrt{\sqrt{\rho_1}\rho_2\sqrt{\rho_1}}\right)^2. \tag{3.10}$$

and $\tilde{\rho}$ is the eigenstate of $\tilde{H}$[1].

We have defined (see definition 24) that ρ is *energy incoherent* if it is a convex combination of eigenstates of H. In this chapter, we will focus on the distillation process from N independent initial systems to arbitrary target systems, e.g., to $\tilde{N}$ independent target systems as illustrated in Fig. 3.2. In particular, we will be interested in the asymptotic behaviour for large N. Thus, our distillation setting is specified by a family of initial and target systems indexed by a natural number N. For each fixed N, the initial system (ρ^N, H^N) consists of N non-interacting subsystems with the total Hamiltonian H^N and a state ρ^N given by

$$H^N = \sum_{n=1}^{N} H_n^N, \qquad \rho^N = \bigotimes_{n=1}^{N}\rho_n^N, \tag{3.11}$$

while the target system is described by an arbitrary Hamiltonian $\tilde{H}^N$ and a state $\tilde{\rho}^N = |\tilde{E}_k^N\rangle\langle\tilde{E}_k^N|$, with $|\tilde{E}_k^N\rangle$ being an eigenstate of $\tilde{H}^N$ corresponding to some energy $\tilde{E}_k^N$. Note that since $\tilde{H}^N$ is arbitrary, it does not need to describe N particles; in fact, it can even be a Hamiltonian of a single qubit.

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[1] In fact, all of our results can be applied to a slightly more general scenario where target states are proportional to the Gibbs state on their support, e.g. for $\tilde{\rho} = \frac{\tilde{\gamma}_k}{\tilde{\gamma}_k+\tilde{\gamma}_l}|\tilde{E}_k\rangle\langle\tilde{E}_k| + \frac{\tilde{\gamma}_l}{\tilde{\gamma}_k+\tilde{\gamma}_l}|\tilde{E}_l\rangle\langle\tilde{E}_l|$, where $|\tilde{E}_i\rangle$ describes the eigenstate of $\tilde{H}$ and $\tilde{\gamma}_i$ is its thermal population.

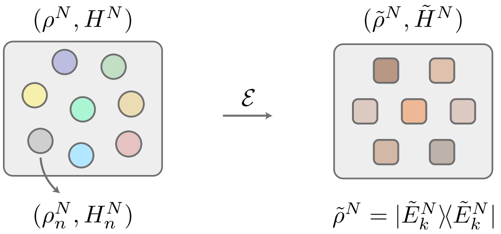

Figure 3.2: **Thermodynamic distillation process.** The presence of a thermal operation is illustrated by the arrow, that converts N independent initial systems into $\tilde{N}$ independent target systems. The initial and target systems are indicated by circles and squares respectively, denoting that each subsystem is defined by a unique Hamiltonian and is initialized in a different state.

An instance of this scenario commonly arises when the original and objective systems are composed of identical, independent subsystems. In this case, the initial system family is denoted by H^N, where $H_n^N = H$, and $\rho^N = \rho^{\otimes N}$. The target system family, on the other hand, consists of $\tilde{N}$ subsystems, with each subsystem characterized by a Hamiltonian $\tilde{H}$ and a state $|\tilde{E}_k\rangle\langle\tilde{E}_k|$. The objective is to identify the optimal distillation rate $\tilde{N}/N$ as N approaches infinity. However, we will also examine a more general case where the subsystems may differ in both their Hamiltonian and state, provided that the initial state is not correlated.

3.3.2 Work extraction

We have described the notion of work extraction in the resource theoretic framework at a length in subsection 2.4.3 of chapter 2. There we have understood that one of the implications of the second law of thermodynamics is that when a system interacts with a thermal bath in equilibrium, the maximum work it can perform (or the maximum amount of work that can be extracted from the system) is limited by the difference ΔF between its initial and final free energy. Traditionally, free energy $F = U - S/\beta$ has only been defined for states at thermal equilibrium, with U representing the internal energy and S denoting the entropy of the system. However, by considering its operational interpretation, one can broaden its definition to investigate non-equilibrium states as well. We have defined the relative entropy as

$$D(\rho\|\gamma) := \mathrm{Tr}\left(\rho(\log\rho - \log\gamma)\right), \tag{3.12}$$

can be interpreted as a non-equilibrium generalisation of the free energy difference between a state ρ and a thermal state γ. It quantifies the maximum amount of work that can be extracted on average from the system in an out-of-equilibrium state [109, 110].

We have seen previously (refer to the subsection 2.4.3 of chapter 2) that work extraction protocols in the resource theoretic framework typically involve altering the external parameters that define the system's Hamiltonian [81, 87]. However, in a resource-theoretic

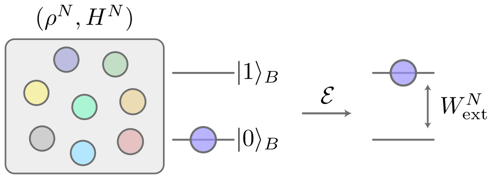

Figure 3.3: **Work extraction process.** The extraction of work W_{ext}^N from a collection of N subsystems, which are in a state ρ^N and described by the Hamiltonian H^N, can be viewed as a specific instance of a thermodynamic distillation process $\mathcal{E}$, which involves a battery system B. The battery is represented by a two-level system with energy levels $|0\rangle_B$ and $|1\rangle B$, corresponding to energies 0 and W_{ext}^N, respectively. In the starting system, we have the N subsystems of interest alongside the battery in the ground state $|0\rangle_B$, whereas the target system only comprises the battery in the excited state $|1\rangle_B$.

treatment [33, 79], external intervention is avoided, and instead, the ancillary work storage or *battery system* B is modelled explicitly. The objective is to convert the battery system from an initial pure energy state to another pure energy state with a higher energy level, as shown in Fig. 3.3. The Hamiltonian of work storage is usually continuous, but a discrete spectrum can also be chosen as long as its energy differences correspond to the amount of work to be extracted. For convenience, we consider a two-level battery system described by a Hamiltonian H_B^N with eigenstates $|0\rangle_B$ and $|1\rangle_B$, that correspond to energies 0 and W_{ext}^N, respectively. The possibility of extracting work equal to W_{ext}^N from N subsystems that are described by a Hamiltonian H^N and prepared in a state ρ^N, is equivalent to the existence of a thermodynamic distillation process that satisfies

$$\mathcal{E}(\rho^N \otimes |0\rangle\langle 0|_B) = |1\rangle\langle 1|_B. \tag{3.13}$$

This distillation process takes $N+1$ initial subsystems described by a Hamiltonian $H^N + H_B^N$ to a target subsystem with a Hamiltonian H_B^N. If only an ϵ-approximate distillation with transformation error ϵ_N is possible, then ϵ_N measures the quality of the extracted work directly. With probability $1 - \epsilon_N$, the battery system ends up in an excited state of energy W_{ext}^N. (It is worth noting that in subsection 2.4.3.2, we have considered this exact scenario where the final state of the N subsystems transformed to Gibbs state. But this doesn't affect the description of work extraction and its analysis.)

3.3.3 Information erasure

The relationship between thermodynamics and information dates back to the inception of thermodynamic theory, illustrated by Maxwell's demon [111]. The thought experiment demonstrated that one could hypothetically decrease the entropy of a gas of particles without investing work by obtaining information about their positions and momenta. Thus, it results an apparent violation of the second law of thermodynamics. Another example, the Szilard engine [85] that highlights the thermodynamic significance of information by

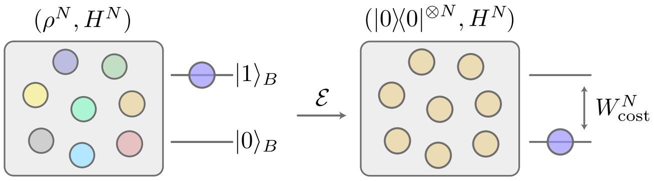

Figure 3.4: **Information erasure.** In order to erase N bits of information, we consider N subsystems that are in the state ρ^N and have a trivial Hamiltonian H^N. The erasure operation is executed by connecting a battery system B that is initially in the excited state $|1\rangle_B$ with energy W^N_{cost}, which represents the energetic expense of the erasure. The erasure procedure resets the state of the N subsystems from ρ^N to a fixed state $|0\rangle^{\otimes N}$ and de-excites the battery system.

converting it into work. Similar to the Maxwell demon, the Szilard engine can also breach the second law if there is some information about the system's state. This puzzle reveals that thermodynamics imposes physical constraints on information processing. In particular, the second law can be reformulated as a statement that no thermodynamic process can result solely in the erasure of information. Each information erasure comes with a fundamental heat cost, leading to an increase in entropy in the environment [73]. Landauer's principle [18] tells us that the erasure process has an unavoidable energetic cost, with the minimum possible amount of energy required to erase a completely an unknown bit of information is given by $\log 2/\beta$. However, in this context a more nuanced view of the Szilard engine and Landauer's erasure is presented in [112].

Just like the process of work extraction, the process of erasure can also be seen as a thermodynamic distillation process. When one wants to erase a set of N bits of information, it can be represented by N two-level systems in a state ρ^N, with a trivial Hamiltonian. In order to measure the energetic cost of erasure, we add a two-level battery system B, which is initially in an excited state $|1\rangle_B$ with energy W^N_{cost}. Then, the erasure process results resetting the state ρ^N to a fixed state $|0\rangle^{\otimes N}$ consumes W^N_{cost} work. The erasure process is possible if there exists the following distillation process:

$$\mathcal{E}(\rho^N \otimes |1\rangle\langle 1|_B) = |0\rangle\langle 0|^{\otimes N} \otimes |0\rangle\langle 0|_B\,, \tag{3.14}$$

with the initial and target Hamiltonians being identical. The transformation error quantifies the quality of erasure, and the process is illustrated in Fig. 3.4.

3.3.4 Thermodynamically-free communication

The intersection of thermodynamics and information theory also allows for the study of the thermodynamic aspects of communication. In a classical communication scenario, Alice aims to encode and transmit classical information to Bob over a quantum channel, which typically involves three steps [113]. Initially, she encodes a message $m \in 1, ..., M$ by prepar-

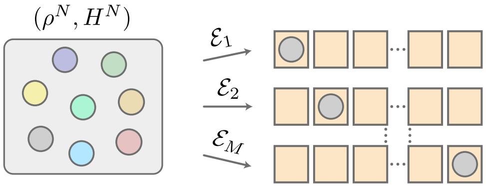

Figure 3.5: **Thermodynamically-free encoding.** Thermal encoding of information involves a thermodynamic distillation process that utilizes N independent subsystems in a state ρ^N with a Hamiltonian H^N as the information carrier. The sender then applies a thermal operation $\mathcal{E}_m$ to encode a message $m \in \{1, ..., M\}$ by transforming ρ^N into nearly distinguishable states. To decode the original message, the receiver performs a measurement on $\mathcal{E}_m(\rho^N)$.

ing a quantum system in a state ρ_m. Next, she sends it to Bob through a noisy quantum channel $\mathcal{N}$. Finally, Bob decodes the original message by performing an optimal measurement on $\mathcal{N}(\rho_m)$. It is important to note that in this standard scenario, both Alice and Bob have complete freedom to use all encoding and decoding methods without any constraints. The only thing beyond their control is the noisy channel $\mathcal{N}$.

In the recent work [114, 115], a modification of this scenario has been introduced, enabling one to quantify the thermodynamic expenditure of communication in a precise manner. To be more specific, it is presumed that Alice and Bob are connected by an error-free channel, and Bob's decoding remains unconstrained. However, Alice is limited to employ solely *thermodynamically-free encodings*. It implies that encoded states ρ_m can only arise from thermal operations performed on a given initial state ρ, that is recognized as an *information carrier*. This signifies that Alice complies with the second law of thermodynamics, where the encoding channel is restricted to utilize no thermodynamic resources except the ones that are already present in the information carrier ρ. This process is illustrated in Fig. 3.5.

The central question is: what is the maximum number of messages $M(\rho, \epsilon_{\mathrm{d}})$ that can be encoded into ρ in a thermodynamically-free manner, such that the average decoding error is less than ϵ_{d}? In this chapter, we will investigate the scene where the information carrier constitutes N independent systems in a state ρ^N, characterized by a Hamiltonian H^N as demonstrated in Eq. (3.11). Equivalently, instead of analyzing $M(\rho^N, \epsilon_{\mathrm{d}})$, we can ask about the optimal encoding rate:

$$R(\rho^N, \epsilon_{\mathrm{d}}) := \frac{\log[M(\rho^N, \epsilon_{\mathrm{d}})]}{N}, . \tag{3.15}$$

In this regard, we will later explain that the optimal thermodynamically-free encodings that allows the optimal rate R to be achieved. We shall show optimal thermodynamical free encoding can be designed by a thermodynamic distillation process. As a consequence, this will allow us to establish a second-order asymptotic expansion of $R(\rho^N, \epsilon_{\mathrm{d}})$ for large N.

3.3.5 Information-theoretic notions and their thermodynamic interpretation

Before we present the results, let us introduce the crucial information-theoretic quantities alongside their thermodynamic interpretations. For any d-dimensional quantum state ρ, we define the relative entropy D between ρ and a thermal Gibbs state γ, along with the relative entropy variance V and the function Y associated with relative entropy skewness [63, 116, 117, 118]:

$$D(\rho\|\gamma) := \mathrm{Tr}\left(\rho\left(\log\rho - \log\gamma\right)\right), \tag{3.16a}$$

$$V(\rho\|\gamma) := \mathrm{Tr}\left(\rho\left(\log\rho - \log\gamma - D(\rho\|\gamma)\right)^2\right), \tag{3.16b}$$

$$Y(\rho\|\gamma) := \mathrm{Tr}\left(\rho\left|\log\rho - \log\gamma - D(\rho\|\gamma)\right|^3\right). \tag{3.16c}$$

It is evident from the aforementioned definitions that we are dealing with the mean, variance, and the absolute third moment of the *operator*

$$\log\rho - \log\gamma \tag{3.17}$$

The average of this random variable, $D(\rho\|\gamma)$, can be construed as the non-equilibrium free energy of the system since

$$\frac{1}{\beta}D(\rho\|\gamma) = \mathrm{Tr}\left(\rho H\right) - \frac{S(\rho)}{\beta} + \frac{\log Z}{\beta}, \tag{3.18}$$

where

$$S(\rho) := -\,\mathrm{Tr}\left(\rho\log\rho\right) \tag{3.19}$$

represents the von Neumann entropy. The higher order moments beyond the average can be interpreted as the fluctuations of the non-equilibrium free energy content of the system. That can be understood most clearly for pure states $\rho = |\psi\rangle\langle\psi|$, where V describes fluctuations of energy of the system:

$$\frac{1}{\beta^2}V(|\psi\rangle\langle\psi|\|\gamma) = \langle\psi|H^2|\psi\rangle - \langle\psi|H|\psi\rangle^2. \tag{3.20}$$

When $\rho = \gamma'$, i.e ρ corresponds to a thermal distribution at a different temperature $T' \neq T$, the expression for V reduces to [63]:

$$V(\gamma'\|\gamma) = \left(1 - \frac{T'}{T}\right)^2 \cdot \frac{c_{T'}}{k_B}, \quad \text{where} \quad c_{T'} = \frac{\partial}{\partial T'}\mathrm{Tr}(H\gamma'), \tag{3.21}$$

such that $c_{T'}$ is the specific heat capacity of the system in a thermal state at temperature T', and k_B is the Boltzmann constant. Now, for the initial system (ρ^N, H^N), we introduce the following notation for free energy and free energy fluctuations:

$$F^N := \frac{1}{\beta}\sum_{n=1}^{N} D(\rho_n^N\|\gamma_n^N), \tag{3.22a}$$

$$\sigma^2(F^N) := \frac{1}{\beta^2}\sum_{n=1}^{N} V(\rho_n^N\|\gamma_n^N), \tag{3.22b}$$

$$\kappa^3(F^N) := \frac{1}{\beta^3}\sum_{n=1}^{N} Y(\rho_n^N\|\gamma_n^N). \tag{3.22c}$$

We also introduce

$$\Delta F^N := \frac{1}{\beta}\left(\sum_{n=1}^{N} D(\rho_n^N\|\gamma_n^N) - D(\tilde{\rho}^N\|\tilde{\gamma}^N)\right), \tag{3.23}$$

which describes the free energy difference between the initial and target states, as well as

$$F_{\text{diss}}^N := \frac{1}{\beta}\left(\sum_{n=1}^{N} D(\rho_n^N\|\gamma_n^N) - D(\rho_{\text{fin}}^N\|\tilde{\gamma}^N)\right), \tag{3.24}$$

which quantifies the amount of free energy that is dissipated in the distillation process, i.e., the free energy difference between the initial and final states.

We would like to make two final technical remarks. Firstly, we will only consider initial systems for which the limits of $\sigma^2(F^N)/N$ and $\kappa^3(F^N)/N$ as $N \to \infty$ exist and are non-zero. Secondly, we will use a shorthand notation throughout the following sections where $\simeq$, $\lesssim$, and $\gtrsim$ denote equalities and inequalities that hold up to terms of order $o(\sqrt{N})$.

3.4 Results

3.4.1 Optimal distillation error and fluctuation-dissipation relations

We present our first set of main results that focus on the thermodynamic distillation process from energy incoherent systems. These two theorems establish a connection between the optimal distillation error and the fluctuations of free energy of the system's initial state, as well as the minimum amount of free energy dissipated in the distillation process due to these fluctuations.

Theorem 26A (Optimal distillation error for incoherent states). *In a distillation scenario with energy incoherent states, the optimal ϵ-approximate distillation process in the asymptotic limit can be characterized by the transformation error ϵ_N, which is given by the equation:*

$$\lim_{N\to\infty} \epsilon_N = \lim_{N\to\infty} \Phi\left(-\frac{\Delta F^N}{\sigma(F^N)}\right), \tag{3.25}$$

where Φ represents the cumulative normal distribution function. Additionally, there exists an ϵ-approximate distillation process for any N with transformation error ϵ_N bounded as follows:

$$\epsilon_N \leq \Phi\left(-\frac{\Delta F^N}{\sigma(F^N)}\right) + \frac{C\kappa^3(F^N)}{\sigma^3(F^N)}, \tag{3.26}$$

Here, C denotes a constant from the Berry-Esseen theorem, which is confined within the bounds:

$$0.4097 \leq C \leq 0.4748. \tag{3.27}$$

Theorem 26B (Fluctuation-dissipation relation for incoherent states)**.** *The minimal free energy dissipated in the optimal distillation process from identical incoherent states that minimize the transformation error ϵ, described by the following relation in the asymptotic limit:*

$$F^N_{\text{diss}} \simeq a(\epsilon_N)\sigma(F^N), \tag{3.28}$$

Here, $a(\epsilon)$ is a function of ϵ given by

$$a(\epsilon) = -\Phi^{-1}(\epsilon)(1-\epsilon) + \frac{\exp\left(\frac{-(\Phi^{-1}(\epsilon))^2}{2}\right)}{\sqrt{2\pi}} \tag{3.29}$$

In the equation, Φ^{-1} represents the inverse function of the cumulative normal distribution function Φ.

In section 3.5.2 and section 3.5.3, we will provide the proofs for the above theorems. In this section, we will briefly discuss the implications and the range of applicability of these theorems. We start by noting that by combining Eq. (3.25) and Eq. (3.28), one can determine the optimal amount of free energy as a function of ΔF^N and $\sigma(F^N)$:

$$F^N_{\text{diss}} \simeq \left(1 - \Phi\left(-\frac{\Delta F^N}{\sigma(F^N)}\right)\right)\Delta F^N + \frac{\exp\left(-\frac{(\Delta F^N)^2}{2\sigma^2(F^N)}\right)}{\sqrt{2\pi}}\sigma(F^N). \tag{3.30}$$

Now, for the analysed case of independent initial subsystems, free energy fluctuations $\sigma(F^N)$ scale as $\sqrt{N}$. Thus, we can classify three regimes, depending on how the free energy difference between the initial and target states, ΔF^N, behaves with increasing N:

$$\lim_{N\to\infty} \frac{\Delta F^N}{\sqrt{N}} = \begin{cases} \infty, \\ -\infty, \\ \alpha \in \mathbb{R}. \end{cases} \tag{3.31}$$

Let us consider the implications of the three regimes in more detail. In the first case, when the free energy of the target state is much smaller than that of the initial state, the transformation error approaches zero in the asymptotic limit as can be seen from Eq. (3.25).

In addition, according to Eq. (3.30) the amount of dissipated free energy F_{diss}^N is approximately equal to the free energy difference between the initial and target states, up to second-order asymptotic terms. This indicates that one can approach the target state arbitrarily closely having much less free energy than the initial state. In the second case, when the free energy of the target state is much larger than that of the initial state, the transformation error approaches one in the asymptotic limit, and the amount of dissipated free energy F_{diss}^N approaches zero. This means that it is almost impossible to approach the target state with much higher free energy than the initial state, and therefore the optimal process is to do nothing. That is why there is no disspation of free energy.

Finally, the third case that is at the core of theorems 26A and 26B. This regime corresponds to the target state having free energy very close to that of the initial state (again, the scale is set by the magnitude of free energy fluctuations). Our theorems then provides the direct correspondence between the optimal transformation error as well as the minimal amount of dissipated free energy in the process and the free energy fluctuations present in the initial state of the system. We can comprehend from Eq. (3.25), for two processes with the same free energy difference ΔF^N, the process involving the initial state with smaller fluctuations will yield a smaller transformation error. Similarly, since the derivative of Eq. (3.30) over $\sigma(F^N)$ for a fixed ΔF^N is always positive, states with smaller free energy fluctuations will lead to smaller free energy dissipation. In particular, consider the example of a battery-assisted distillation process, i.e. a thermodynamic transformation from $(\rho^N \otimes |1\rangle\langle 1|_B, H^N + H_B)$ to $(\tilde{\rho}^N \otimes |0\rangle\langle 0|_B, H^N + H_B)$, where the energy gap of the battery system B is W_{cost}^N. Now, the quality of transformation from ρ^N to $\tilde{\rho}^N$ (measured by transformation error ϵ_N) depends on the amount of work W_{cost}^N that we invest into the process. As expected, to achieve $\epsilon \leq 1/2$, we need to invest at least the difference of free energies $[D(\tilde{\rho}^N \| \tilde{\gamma}^N) - D(\rho^N \| \gamma^N)]/\beta$. However, theorem 26A tells us how much more work is required to reduce the transformation error to a desired level: the more free energy fluctuations there were in ρ^N, the more work we need to provide.

Let us compare theorem 26A and 26B to the results presented in the article by Chubb et. al. [63] that focuses on the incoherent thermodynamic interconversion between identical copies of the initial system, $\rho^{\otimes N}$, and identical copies of the target system, $\tilde{\rho}^{\otimes \tilde{N}}$. Though our results were limited to the case of the target state being an eigenstate of the target Hamiltonian, our findings demonstrate a significant advancement in multiple directions.

- Firstly, our results apply to general independent systems rather than identical copies exclusively.
- Secondly, our theorems account for cases where the Hamiltonians of the initial and target systems can differ, making our work highly applicable to processes such as work extraction or thermodynamically-free communication.
- Thirdly, we have surpassed the second-order asymptotic result by providing a single-

shot upper bound on the optimal transformation error, ϵ_N, which is expressed in Eq. (3.26) and holds for any finite N. As a result, it is possible to obtain a guarantee on the transformation error in the finite N regime that approaches the asymptotically optimal value as $N \to \infty$.

- Finally, we have derived the expression for the actual amount of dissipated free energy in the optimal process, and related it to the fluctuations of the free energy content of the initial state.

Our second pair of main results is analogous to the first pair, but concerns thermodynamic distillation process from N identical copies of a pure quantum system. Thus, the following two theorems connect the optimal distillation error to the free energy fluctuations of the initial state of the system, and the minimal amount of free energy dissipated in such a distillation process to these fluctuations. To formally express these theorems, we introduce a technical notion of a Hamiltonian with an *incommensurable* spectrum. This Hamiltonian is such that for any two energy levels, E_i and E_j, the ratio between E_i and E_j can not be rational. We then have the following results.

Theorem 27A (Optimal distillation error for identical pure states)**.** *In a distillation scenario where N identical initial systems are each in a pure state $|\psi\rangle\langle\psi|$ and have the same Hamiltonian H with incommensurable spectrum, the optimal ϵ-approximate distillation process has a transformation error ϵ_N that asymptotically satisfies*

$$\lim_{N\to\infty} \epsilon_N = \lim_{N\to\infty} \Phi\left(-\frac{\Delta F^N}{\sigma(F^N)}\right), \tag{3.32}$$

where Φ represents the cumulative normal distribution function. Additionally, this result remains valid even if both the initial and target systems are extended by an ancillary system with an arbitrary Hamiltonian H_A, where the initial and target states are eigenstates of H_A.

Theorem 27B (Fluctuation-dissipation relation for identical pure states)**.** *In the optimal distillation process that minimizes the transformation error ϵ for N identical pure states, the amount of free energy dissipated asymptotically satisfies*

$$F^N_{\text{diss}} \gtrsim a(\epsilon_N)\sigma(F^N), \tag{3.33}$$

where $a(\epsilon)$ is defined in Eq. (3.29).

In sections 3.5.4 and 3.5.5, we provide the proofs for the aforementioned theorems. However, we would like to add one comment to the previous discussion. In the case of a pure state, the free energy fluctuations are equivalent to the energy fluctuations (as demonstrated in Eq. (3.20)). Moreover, given that all pure states are identical in the scenario we

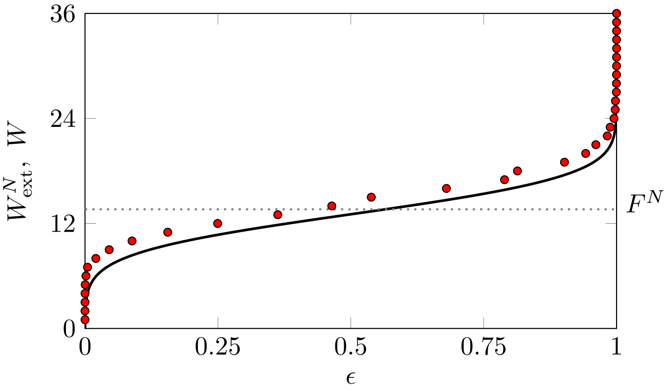

Figure 3.6: **Optimal work extraction.** This diagram compares the asymptotic approximation, given by Eq.(3.38), with the actual optimal value W (represented by red circles) for the amount of extracted work W_{ext}^N as a function of transformation error ϵ. To obtain the optimal value, the thermomajorisation conditions were explicitly solved, and details about this process are available in section 3.5.1. The temperature of the thermal bath is set to $\beta = 1$, and the initial system comprises 100 two-level subsystems. The first 59 subsystems are in a thermal state of $0.6|0\rangle\langle 0| + 0.4|1\rangle\langle 1|$, while the remaining 41 subsystems are in a thermal state of $0.75|0\rangle\langle 0| + 0.25|1\rangle\langle 1|$. The initial state of the system is composed of 59 copies of $0.9|0\rangle\langle 0| + 0.1|1\rangle\langle 1|$ and 41 copies of $0.7|0\rangle\langle 0| + 0.3|1\rangle\langle 1|$. The non-equilibrium free energy of the total initial system, F^N, is shown as a grey dotted line.

are considering, we can simplify the expression as follows:

$$\frac{1}{N}\sigma^2(F^N) = \langle H^2\rangle_\psi - \langle H\rangle_\psi^2, \tag{3.34}$$

where we use the shorthand notation $\langle \cdot \rangle_\psi = \langle\psi| \cdot |\psi\rangle$. Similar to the incoherent case, the optimal transformation error exhibits non-trivial behavior only when $\Delta F^N \simeq \alpha\sqrt{N}$, and its value is determined by the ratio

$$\frac{\alpha}{\sqrt{(\langle H^2\rangle_\psi - \langle H\rangle_\psi^2)}}. \tag{3.35}$$

3.4.2 Optimal work extraction

We will now discuss the first application of our theorems, which focuses on the work extraction from a collection of N non-interacting subsystems, each of which has a Hamiltonian H_n^N and is in an incoherent state ρ_n^N. This work extraction process is a particular instance of thermodynamic distillation, as previously described in section 3.3.2. It is important to note that the pure battery state does not contribute to the fluctuations σ and κ, and that the difference between the non-equilibrium free energies of the ground and excited battery states is simply the energy difference W_{ext}^N. Then, theorem 26A tells us that, in the asymptotic limit, the optimal transformation error for extracting the amount of work W_{ext}^N is

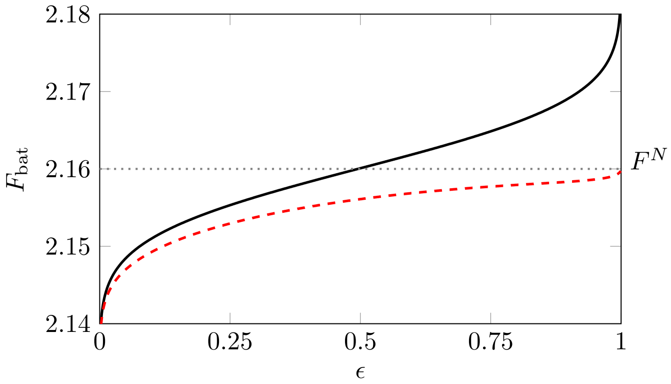

Figure 3.7: **Work quality.** Non-equilibrium free energy F_{bat} of the two-level battery system calculated for the final (dashed red line) and target (solid black line) state of the optimal work extraction process. The inverse temperature of the thermal bath is chosen to be $\beta = 1$, and the initial state that the work is extracted from is composed of 100 copies of a state 0.7$|0\rangle\langle 0|$+0.3$|1\rangle\langle 1|$. Each subsystem is described by the Hamiltonian corresponding to a thermal state 0.6$|0\rangle\langle 0|$+0.4$|1\rangle\langle 1|$ and the non-equilibrium free energy of the total initial system, F^N, is indicated by a grey dotted line.

$$\lim_{N\to\infty} \epsilon_N = \lim_{N\to\infty} \Phi\left(\frac{W_{\text{ext}}^N - F^N}{\sigma(F^N)}\right). \tag{3.36}$$

The difference $(W_{\text{ext}}^N - F^N)$ once again gives rise to three cases. In order for the asymptotic error to be different from zero and one, the extracted work W_{ext}^N must be in the form

$$W_{\text{ext}}^N \simeq F^N - \alpha\sqrt{N}, \tag{3.37}$$

where α is a constant. Substituting this into the previous equation Eq. (3.36) gives us the second-order asymptotic expression for the extracted work:

$$W_{\text{ext}}^N \simeq F^N + \sigma(F^N)\Phi^{-1}(\epsilon). \tag{3.38}$$

Thus, for a fixed quality of extracted work measured by ϵ, greater amount of work can be extracted from states with smaller free energy fluctuations (assuming that the initial free energy F^N is fixed). This is a direct generalisation of the result obtained in [63] to a scenario with non-identical initial systems and with a clearer interpretation of the error in the battery system. Here, we present a comparison between our bounds and the numerically optimised work extraction processes in Fig. 3.6.

Similarly, using theorem 27A, we can calculate the optimal work extraction process from a group of N non-interacting subsystems having identical Hamiltonians H and each in the identically same pure state $|\psi\rangle\langle\psi|$. To achieve this, we select the ancillary system A to be the battery B with energy splitting W_{ext}^N, and having the initial and target states as $|0\rangle_B$ and $|1\rangle_B$. Since all systems are in identical pure states and described by the same Hamiltonian, we have $\sigma(F^N)$ is specified by Eq. (3.34) and

$$\frac{1}{N}F^N = \langle H\rangle_\psi + \frac{\log Z}{\beta}. \tag{3.39}$$

Therefore, the optimal amount of work that can be extracted from N pure quantum systems up to the second-order asymptotic expansion can be expressed as follows:

$$W\text{ext} \simeq N\left(\langle H\rangle_\psi + \frac{\log Z}{\beta} + \frac{\langle H^2\rangle_\psi - \langle H\rangle_\psi^2}{\sqrt{N}}\Phi^{-1}(\epsilon)\right). \tag{3.40}$$

In conclusion, theorem 26B (and to some extent theorem 27B) can be utilized to explore the meaning of work quality, which is quantified by the transformation error ϵ. So far, we have evaluated the amount of extracted work as the difference between the free energy of the initial state of the battery and its target state, which was achieved with a probability of success of $1-\epsilon$. However, as per the aforementioned theorems, the free energy of the final state of the battery can be precisely determined, providing a more accurate amount of the extracted work (without any error). Fig. 3.7 illustrates the trend of both measures as a function of ϵ, indicating that the two concepts coincide when the error ϵ is small.

3.4.3 Optimal cost of erasure

To determine the optimal work cost for erasing N two-level systems that are initially in incoherent states ρ_n^N, we employ theorem 26A, following a similar approach to the previous section, but tailored to the situation described in section 3.3.3. As a result, we obtain the optimal transformation error in the erasure process expressed as:

$$\lim_{N\to\infty} \epsilon_N = \lim_{N\to\infty} \Phi\left(\frac{\frac{1}{\beta}S(\rho^N) - W_{\text{cost}}^N}{\sigma(F^N)}\right), \tag{3.41}$$

Here, $S(\rho^N)$ is the von Neuman entropy of the initial state, and W_{cost}^N is the minimum work cost required. By following a similar rationale to the previous case of work extraction, we can derive the second-order asymptotics for the cost of erasure:

$$W_{\text{cost}}^N \simeq \frac{S(\rho^N)}{\beta} - \sigma(F^N)\Phi^{-1}(\epsilon). \tag{3.42}$$

We would like to make three brief comments regarding the aforementioned result. Firstly, we only examined the incoherent result, theorem 26A, as in the case of trivial Hamiltonians, the erasure of a pure state $|\psi\rangle\langle\psi|^{\otimes N}$ is free (since all unitary transformations will then be thermodynamically-free). While our results are easily extends to the scenario for non-trivial Hamiltonians, we believe that the simple case we outlined above is the most informative and restores the core of Landauer's original erasure scenario. Secondly, since the maximally mixed initial state has zero free energy fluctuations ($\sigma(F^N) = 0$), we cannot directly use our result (which connects fluctuations of initial state with dissipation) to obtain the erasure cost of N completely unknown bits of information. However, by utilizing the techniques presented in section 3.5, it is simple to demonstrate that in this scenario, the exact expression (applicable for all N) for the erasure cost is given by

$$W_{\text{cost}}^N = \frac{N}{\beta}\left(\log 2 - \frac{\log(1-\epsilon)}{N}\right). \tag{3.43}$$

Thus, if the error is zero, Landauer's erasure cost is recovered [119]. Thirdly, similar to the case of work extraction, theorem 26B can also be employed here to examine the significance of erasure quality, which is determined by ϵ.

3.4.4 Optimal thermodynamically-free communication rate

In this section, we describe how theorems 26A and 27A can be used to determine the optimal thermodynamically-free encoding rate for a collection of N identical subsystems in either incoherent or pure states. To accomplish this, we select the target system consisting of a single M-dimensional quantum system with a trivial Hamiltonian $\tilde{H} = 0$, prepared in any of the degenerate eigenstates of $\tilde{H}$. It should be noted that the non-equilibrium free energy of such a target system is expressed by the equation

$$\frac{1}{\beta}D(\tilde{\rho}^N\|\tilde{\gamma}^N) = \frac{1}{\beta}\log M. \tag{3.44}$$

According to our theorems, in the asymptotic limit, the optimal transformation error ϵ in the distillation process can be determined by the equation

$$\lim_{N\to\infty}\epsilon_N = \lim_{N\to\infty}\Phi\left(\frac{\frac{1}{\beta}\log M - F^N}{\sigma(F^N)}\right). \tag{3.45}$$

Upon rewriting the above equation, we obtain the second-order asymptotic behaviour as follows:

$$\log M \simeq \beta F^N + \beta\sigma(F^N)\Phi^{-1}(\epsilon). \tag{3.46}$$

Now, the distillation process above can be followed by unitaries that map between M degenerate eigenstates of $\tilde{H}$ that we will simply denote $|1\rangle, \dots, |M\rangle$. It is important to note that such unitaries are thermodynamically-free because they operate in a fixed energy subspace. This protocol enables the encoding of M messages into M states σ_i, with each state being ϵ-close in infidelity distance to $|i\rangle$ for $i \in 1, \dots, M$. Decoding the message involves performing a measurement in the eigenbasis of $\tilde{H}$, resulting in the average decoding error

$\epsilon_{\rm d}$ satisfying the following relation:

$$1-\epsilon_{\rm d} := \frac{1}{M}\sum_{i=1}^{M} \langle i|\,\sigma_i\,|i\rangle = 1-\epsilon, \tag{3.47}$$

that implies that $\epsilon_{\rm d} = \epsilon$

By using the communication protocol described above, we can derive the following asymptotic lower bound on the optimal thermodynamically-free encoding rate into a state ρ^N (as shown in Eq. (3.15)):

$$R(\rho^N,\epsilon_{\rm d}) \geq \frac{\beta}{N}(F^N + \sigma(F^N)\Phi^{-1}(\epsilon_{\rm d})) + o\left(\frac{1}{\sqrt{N}}\right). \tag{3.48}$$

The lower bound presented above matches exactly with the upper bound for $R(\rho^N,\epsilon_{\rm d})$ that was recently derived in [115], albeit for a slightly different scenario. In [115], the lower and upper bounds were derived for the case when $\rho_n^N = \rho$ and $H_n^N = H$ for all n, with $\tilde{H}^N = H^N$, and with Gibbs-preserving operations instead of thermal operations. However, the proof presented in [115] can be easily adapted to the current scenario, keeping the first restriction that the initial state is $\rho^N = \rho^{\otimes N}$ and all initial subsystems have equal Hamiltonians. We provide detailed explanation on how to adapt the proof in appendix 6.2. Furthermore, we also discuss a technical result concerning hypothesis testing relative entropy, which needs to be proven in order to make the proof work when subsystems are not identical. Here we conclude that

$$R(\rho^{\otimes N},\epsilon_{\rm d}) = D(\rho\|\gamma) + \frac{\sqrt{V(\rho\|\gamma)}}{\sqrt{N}}\Phi^{-1}(\epsilon_{\rm d}) + o\left(\frac{1}{\sqrt{N}}\right), \tag{3.49}$$

where ρ is either a pure or incoherent state.

The above result has a thermodynamic interpretation as the opposite of the Szilard engine. The Szilard engine converts bits of information into work, whereas the protocol we examine here employs the system's free energy (i.e., its ability to perform work) to encode bits of information. Although the asymptotic result was recently established in Ref. [114], our results demonstrate a deeper relationship, as they link free energy fluctuations to the optimal average decoding error

3.5 Derivation of the results

The subsequent sections begins with an introduction to the mathematical formalism employed to investigate the incoherent distillation process. This formalism is subsequently utilized to establish the proofs of theorems 26A and 26B. Furthermore, we establish theorems 27A and 27B by initially transforming the distillation problem from pure states to an equivalent incoherent problem, and subsequently utilizing the formalism of incoherent distillations.

3.5.1 Incoherent distillation process

3.5.1.1 Distillation conditions via approximate majorisation

Firstly, let us recall the concept of energy incoherent states (refer to definition 24). An energy-incoherent state ρ of a d-dimensional quantum system is defined as one that commutes with the system's Hamiltonian, resulting in a block-diagonal representation in the energy eigenbasis. This state can also be represented by a d-dimensional classical state or probability vector $\boldsymbol{p}$ consisting of the eigenvalues of ρ. The thermal Gibbs state γ is a classic example of an energy-incoherent state, which can be represented by a classical state of thermal occupations $\boldsymbol{\gamma}$. Additionally, a state $|E_k\rangle\langle E_k|$ of energy eigenstate E_k can be represented by a *sharp classical state* $\boldsymbol{s}_k$, where $(\boldsymbol{s}_k)_j = \delta_{jk}$.

To develop the solution to the thermodynamic interconversion for incoherent states, we shall recapitulate two fundamental concepts that we have introduced in chapter 1: *approximate majorisation* and *embedding*. First, given two d-dimensional probability vectors $\boldsymbol{p}$ and $\boldsymbol{q}$, we say that $\boldsymbol{p}$ majorises $\boldsymbol{q}$, and write $\boldsymbol{p} \succ \boldsymbol{q}$, if and only if [14]

$$\forall k: \quad \sum_{j=1}^{k} p_j^{\downarrow} \geq \sum_{j=1}^{k} q_j^{\downarrow}, \tag{3.50}$$

where $\boldsymbol{p}^{\downarrow}$ denotes the vector $\boldsymbol{p}$ rearranged in a decreasing order. Next, we shall introduce a variant of majorisation called *ϵ-post majorisation*.

Definition 28 (ϵ-post majorisation [63]). We say that $\boldsymbol{p}$ ϵ-postmajorises $\boldsymbol{q}$, and write $\boldsymbol{p} \succ_{\epsilon} \boldsymbol{q}$, if $\boldsymbol{p}$ majorises $\boldsymbol{r}$ which is ϵ-close in the infidelity distance to $\boldsymbol{q}$, i.e.,

$$1 - F(\boldsymbol{q}, \boldsymbol{r}) \leq \epsilon, \qquad F(\boldsymbol{q}, \boldsymbol{r}) := \left(\sum_{j=1}^{d} \sqrt{q_j r_j} \right)^2 . \tag{3.51}$$

Second, we express the thermal distribution $\boldsymbol{\gamma}$ as a probability vector with rational entries,

$$\boldsymbol{\gamma} = \left[\frac{D_1}{D}, \ldots, \frac{D_d}{D} \right], \tag{3.52}$$

with D and D_k being integers. Now, the embedding map $\Gamma_{\boldsymbol{\gamma}}$ as we have introduced in subsection 1.4.2.1 of chapter 1, is defined as a transformation that maps a d-dimensional classical state $\boldsymbol{p}$ to a D-dimensional classical state $\hat{\boldsymbol{p}}$ in the following way [34]:

$$\hat{\boldsymbol{p}} = \Bigg[\underbrace{\frac{p_1}{D_1}, \dots, \frac{p_1}{D_1}}_{D_1 \text{ times}}, \dots, \underbrace{\frac{p_d}{D_d}, \dots, \frac{p_d}{D_d}}_{D_d \text{ times}}\Bigg]. \tag{3.53}$$

We will refer to the sets of repeated elements above as *embedding boxes*. Observe that the embedded version of a thermal state $\boldsymbol{\gamma}$ is a *maximally mixed state* over D states,

$$\boldsymbol{\eta} := \frac{1}{D}[1, \dots, 1], \tag{3.54}$$

and the embedded version of a sharp state $\boldsymbol{s}_k$ is a *flat state* $\boldsymbol{f}_k$ that is maximally mixed over a subset of D_k entries, with zeros otherwise:

$$\hat{\boldsymbol{s}}_k = \boldsymbol{f}_k := \Bigg[\underbrace{0, \dots, 0}_{\sum_{j=1}^{k-1} D_j}, \underbrace{1 \dots 1}_{D_k}, \underbrace{0, \dots, 0}_{\sum_{j=k+1}^{d} D_j}\Bigg]. \tag{3.55}$$

We can now state the crucial theorem based on [34] and concerning thermodynamic interconversion for incoherent states.

Theorem 28 (Corollary 7 of [63]). *For the initial and target system with the same thermal distribution $\boldsymbol{\gamma}$, there exists a thermal operation mapping between an energy-incoherent state $\boldsymbol{p}$ and a state ϵ-close to $\boldsymbol{q}$ in infidelity distance, if and only if $\hat{\boldsymbol{p}} \succ_\epsilon \hat{\boldsymbol{q}}$.*

Although we intend to examine the general case of initial and final systems with different Hamiltonians, we can still apply the above theorem with some ingenuity. Specifically, we consider a family of total systems comprising the first N subsystems with initial Hamiltonians H_n^N, while the remaining part is described by the target Hamiltonian $\tilde{H}^N$. The initial states of the total system for the first N subsystems are chosen to be a general product of incoherent states $\boldsymbol{p}_n^N$, while the remaining part is prepared in a thermal equilibrium state $\tilde{\boldsymbol{\gamma}}^N$ corresponding to $\tilde{H}^N$. Because Gibbs states are thermodynamically free, this setup is thermodynamically equivalent to having only the first N systems with Hamiltonians H_n^N and in states $\boldsymbol{p}_n^N$. Moreover, for the target states of the total system, we select thermal equilibrium states $\boldsymbol{\gamma}_n^N$ for the first N subsystems and sharp states $\tilde{\boldsymbol{s}}_k^N$ of the Hamiltonian $\tilde{H}^N$ for the remaining part. Once more, this is thermodynamically equivalent to having just the system with Hamiltonian $\tilde{H}^N$ and in a state $\tilde{\boldsymbol{s}}_k^N$. Thus, employing theorem 28, an ϵ-approximate distillation process for incoherent states exists if and only if:

$$\left(\bigotimes_{n=1}^{N} \hat{\boldsymbol{p}}_n^N \otimes \hat{\tilde{\boldsymbol{\gamma}}}^N\right) \succ_\epsilon \left(\bigotimes_{n=1}^{N} \hat{\boldsymbol{\gamma}}_n^N \otimes \hat{\tilde{\boldsymbol{s}}}_k^N\right). \tag{3.56}$$

This way, using a single fixed Hamiltonian, we can encode transformations between different Hamiltonians.

Let us introduce the following shorthand notation:

$$\hat{\boldsymbol{P}}^N := \bigotimes_{n=1}^{N} \hat{\boldsymbol{p}}_n^N, \qquad \hat{\boldsymbol{G}}^N := \bigotimes_{n=1}^{N} \hat{\boldsymbol{\gamma}}_n^N = \bigotimes_{n=1}^{N} \boldsymbol{\eta}_n^N. \tag{3.57}$$

Therefore, utilizing the previous facts regarding the embedding map, we can assert the following statement: an ϵ-approximate thermodynamic distillation process can occur from N systems described with Hamiltonians H_n^N in energy-incoherent states $\boldsymbol{p}_n^N$ to a system with a Hamiltonian $\tilde{H}^N$ and in a sharp energy eigenstate $\tilde{\boldsymbol{s}}_k^N$ if and only if

$$\hat{\boldsymbol{P}}^N \otimes \tilde{\boldsymbol{\eta}}^N \succ_\epsilon \hat{\boldsymbol{G}}^N \otimes \tilde{\boldsymbol{f}}_k^N. \tag{3.58}$$

3.5.1.2 Information-theoretic intermission

We will take a brief intermission to highlight some important remarks regarding the information-theoretic quantities defined in Eqs. (3.16a)-(3.16c). For incoherent states ρ and γ, which can be represented as classical states $\boldsymbol{p}$ and $\boldsymbol{\gamma}$, these quantities take a simplified classical form, as follows:

$$D(\boldsymbol{p}\|\boldsymbol{\gamma}) := \sum_i p_i \left(\log \frac{p_i}{\gamma_i}\right), \tag{3.59a}$$

$$V(\boldsymbol{p}\|\boldsymbol{\gamma}) := \sum_i p_i \left(\log \frac{p_i}{\gamma_i} - D(\boldsymbol{p}\|\boldsymbol{\gamma})\right)^2, \tag{3.59b}$$

$$Y(\boldsymbol{p}\|\boldsymbol{\gamma}) := \sum_i p_i \left|\log \frac{p_i}{\gamma_i} - D(\boldsymbol{p}\|\boldsymbol{\gamma})\right|^3. \tag{3.59c}$$

Moreover, by doing a simple algebra, one can easily show that the above quantities are invariant under embedding, i.e., $D(\boldsymbol{p}\|\boldsymbol{\gamma}) = D(\hat{\boldsymbol{p}}\|\boldsymbol{\eta})$, and the same holds for V and Y. Therefore

$$D(\boldsymbol{p}\|\boldsymbol{\gamma}) = D(\hat{\boldsymbol{p}}\|\boldsymbol{\eta}) = \log D - H(\hat{\boldsymbol{p}}), \tag{3.60a}$$

$$V(\boldsymbol{p}\|\boldsymbol{\gamma}) = V(\hat{\boldsymbol{p}}\|\boldsymbol{\eta}) = V(\hat{\boldsymbol{p}}), \tag{3.60b}$$

$$Y(\boldsymbol{p}\|\boldsymbol{\gamma}) = Y(\hat{\boldsymbol{p}}\|\boldsymbol{\eta}) = Y(\hat{\boldsymbol{p}}), \tag{3.60c}$$

where

$$H(\boldsymbol{p}) := \sum_i p_i(-\log p_i), \tag{3.61a}$$

$$V(\boldsymbol{p}) := \sum_i p_i(\log p_i + H(\boldsymbol{p}))^2, \tag{3.61b}$$

$$Y(\boldsymbol{p}) := \sum_i p_i \left|\log p_i + H(\boldsymbol{p})\right|^3, \tag{3.61c}$$

and note that $V(\boldsymbol{p}) = 0$ if and only if $\boldsymbol{p}$ is a flat state.

3.5.1.3 Optimal error for a distillation process

To derive an explicit expression for the optimal transformation error from the approximate majorization condition in Eq. (3.58), we begin with the following theorem proven in [63].

Lemma 29 (Lemma 21 of [63])**.** *Let* $\boldsymbol{p}$ *and* $\boldsymbol{q}$ *be distributions with* $V(\boldsymbol{q}) = 0$*. Then*

$$\min\left\{\epsilon | \boldsymbol{p} \succ_\epsilon \boldsymbol{q}\right\} = 1 - \sum_{i=1}^{\exp H(\boldsymbol{q})} p_i^\downarrow. \tag{3.62}$$

Applying the above lemma to Eq. (3.58) leads to the following expression for the optimal error ϵ_N:

$$\epsilon_N = 1 - \sum_{i=1}^{\exp[H(\hat{\boldsymbol{G}}^N)+H(\tilde{\boldsymbol{f}}_k^N)]} \left(\hat{\boldsymbol{P}}^N \otimes \tilde{\boldsymbol{\eta}}^N\right)_i^\downarrow. \tag{3.63}$$

We can make two observations for an arbitrary classical state $\boldsymbol{p}$ and any flat state $\boldsymbol{f}$. Firstly, the size of the support of $\boldsymbol{f}$ is simply $\exp(H(\boldsymbol{f}))$. Secondly, the entries of $\boldsymbol{p} \otimes \boldsymbol{f}$ are the copied and scaled entries of $\boldsymbol{p}$. Thus, we can express the sum of the l largest elements of $\boldsymbol{p}$ as

$$\sum_{i=1}^{l} p_i^\downarrow = \sum_{i=1}^{l\exp(H(\boldsymbol{f}))} (\boldsymbol{p} \otimes \boldsymbol{f})_i^\downarrow. \tag{3.64}$$

Inverting the above expression we can write

$$\sum_{i=1}^{l} (\boldsymbol{p} \otimes \boldsymbol{f})_i^\downarrow = \sum_{i=1}^{l\exp(-H(\boldsymbol{f}))} p_i^\downarrow, \tag{3.65}$$

where the summation with non-integer upper limit x should be interpreted as:

$$\sum_{i=1}^{x} p_i := \sum_{i=1}^{\lfloor x \rfloor} p_i + (x - \lfloor x \rfloor) p_{\lceil x \rceil}. \tag{3.66}$$

Since $\tilde{\boldsymbol{\eta}}$ is a flat state, we conclude that

$$\epsilon_N = 1 - \sum_{i=1}^{\exp[H(\hat{\boldsymbol{G}}^N)+H(\tilde{\boldsymbol{f}}_k^N)-H(\tilde{\boldsymbol{\eta}}^N)]} (\hat{\boldsymbol{P}}^N)_i^\downarrow. \tag{3.67}$$

One can see that the error depends on partial ordered sums as above. In order to deal with such a sum, we introduce the function $\chi_{\boldsymbol{p}}$ defined implicitly by the following relation

$$\sum_{i=1}^{\chi_{\boldsymbol{p}}(l)} p_i^{\downarrow} = \sum_i \{p_i | p_i \geq 1/l\}. \tag{3.68}$$

In other words $\chi_{\boldsymbol{p}}(l)$ counts the number of elements of $\boldsymbol{p}$ that are greater than $1/l$. Now, we have the following lemma that will be important in proving our theorems.

Lemma 30. *Any d-dimensional probability vector $\boldsymbol{p}$ satisfies the following for all $l \in \{1, \ldots, d\}$ and for all $\alpha \geq 1$:*

$$\sum_{i=1}^{l} p_i^{\downarrow} \geq \sum_{i=1}^{\chi_{\boldsymbol{p}}(l)} p_i^{\downarrow}, \tag{3.69a}$$

$$\sum_{i=1}^{l} p_i^{\downarrow} \leq \sum_{i=1}^{\chi_{\boldsymbol{p}}(\alpha l)/c} p_i^{\downarrow}, \tag{3.69b}$$

where

$$c = \sqrt{\alpha} \sum_{i=\chi_{\boldsymbol{p}}(\sqrt{\alpha} l)}^{\chi_{\boldsymbol{p}}(\alpha l)} p_i^{\downarrow}. \tag{3.70}$$

Moreover, as the probabilities are ordered in the sums given in Eq. (3.69a) and Eq. (3.69b), it simply follows that

$$\chi_{\boldsymbol{p}}(l) \leq l \leq \chi_{\boldsymbol{p}}(\alpha l)/c. \tag{3.71}$$

Proof. It is simple to demonstrate the first inequality by observing that the number of entries greater than $1/l$, which is denoted by $\chi_{\boldsymbol{p}}(l)$, can be bounded from above l because of normalization. Moving on to the second inequality, we begin with the following observation:

$$\sum_{i=1}^{\chi_{\boldsymbol{p}}(\sqrt{\alpha} l)} \left(p_i^{\downarrow} - \frac{1}{\sqrt{\alpha} l} \right) \geq \sum_{i=1}^{\chi_{\boldsymbol{p}}(\alpha l)} \left(p_i^{\downarrow} - \frac{1}{\sqrt{\alpha} l} \right), \tag{3.72}$$

that results from the fact that all the extra terms on the right-hand side of the above are negative by definition. By rearranging terms, we arrive at

$$\chi_{\boldsymbol{p}}(\alpha l) - \chi_{\boldsymbol{p}}(\sqrt{\alpha} l) \geq c l, \tag{3.73}$$

that straight-forwardly implies

$$l \leq \frac{\chi_{\boldsymbol{p}}(\alpha l)}{c}. \tag{3.74}$$

□

3.5.2 Proof of theorem 26A

We will prove theorem 26A in two parts. In the first part, we will derive an upper bound for the optimal transformation error ϵ_N and write it as Eq. (3.26). In the second part, we will provide a lower bound for ϵ_N and show that it approaches the upper bound in the asymptotic limit, thus proving Eq. (3.25).

3.5.2.1 Upper bound for the transformation error

We begin by introducing the following averaged entropic quantities for the total initial distribution $\hat{\boldsymbol{P}}^N$:

$$h_N := \frac{1}{N} H(\hat{\boldsymbol{P}}^N) = \frac{1}{N}\sum_{n=1}^{N} H(\hat{\boldsymbol{p}}_n^N) =: \frac{1}{N}\sum_{n=1}^{N} h_n^N, \tag{3.75a}$$

$$v_N := \frac{1}{N} V(\hat{\boldsymbol{P}}^N) = \frac{1}{N}\sum_{n=1}^{N} V(\hat{\boldsymbol{p}}_n^N) =: \frac{1}{N}\sum_{n=1}^{N} v_n^N, \tag{3.75b}$$

$$y_N := \frac{1}{N} Y(\hat{\boldsymbol{P}}^N) = \frac{1}{N}\sum_{n=1}^{N} Y(\hat{\boldsymbol{p}}_n^N) =: \frac{1}{N}\sum_{n=1}^{N} y_n^N. \tag{3.75c}$$

Observe that the above v_N and y_N are, up to rescaling by N/β, incoherent versions of $\sigma^2(F^N)$ and $\kappa^3(F^N)$ defined in Eqs. (3.22b)-(3.22c). We also define the function l:

$$l(z) := \exp\left(N h_N + z\sqrt{N v_N}\right). \tag{3.76}$$

We now rewrite the upper summation limit appearing in Eq. (3.67) employing the above function:

$$\exp[H(\hat{\boldsymbol{G}}^N) + H(\tilde{\boldsymbol{f}}_k^N) - H(\tilde{\boldsymbol{\eta}}^N)] = l(x), \tag{3.77}$$

so that

$$x = \frac{D(\hat{\boldsymbol{P}}^N \| \hat{\boldsymbol{G}}^N) - D(\tilde{\boldsymbol{f}}_k^N \| \tilde{\boldsymbol{\eta}}^N)}{\sqrt{V(\hat{\boldsymbol{P}}^N)}}. \tag{3.78}$$

This can be transformed further by using the invariance property of relative entropic quantities under embedding as per Eqs. (3.60a)-(3.60b) that reduces x in Eq. (3.78) in the following way:

$$x = \frac{\sum_{n=1}^{N} D(\boldsymbol{p}_n^N \| \boldsymbol{\gamma}_n^N) - D(\tilde{\boldsymbol{s}}_k^N \| \tilde{\boldsymbol{\gamma}}^N)}{\left(\sum_{n=1}^{N} V(\boldsymbol{p}_n^N \| \boldsymbol{\gamma}_n^N)\right)^{\frac{1}{2}}}, \tag{3.79}$$

which is precisely the argument of Φ that appeared in the statement of theorem 26A in Eq. (3.25):

$$x = \frac{\Delta F^N}{\sigma(F^N)}. \tag{3.80}$$

We conclude that with the above x we can then rewrite the expression for the optimal transformation error, Eq. (3.67), as

$$\epsilon_N = 1 - \sum_{i=1}^{l(x)} (\hat{\boldsymbol{P}}^N)_i^{\downarrow}. \tag{3.81}$$

Next, we would like to find an upper bound for the error employing Eq. (3.69a):

$$\begin{aligned} \epsilon_N &\leq 1 - \sum_{i=1}^{\chi_{\hat{\boldsymbol{P}}^N}(l(x))} (\hat{\boldsymbol{P}}^N)_i^{\downarrow} \\ &= 1 - \sum_i \left\{ \hat{P}_i^N \middle| \hat{P}_i^N \geq \frac{1}{l(x)} \right\}. \end{aligned} \tag{3.82}$$

In order to evaluate the above sum, consider N discrete random variables X_n taking values $-\log(\hat{\boldsymbol{p}}_n^N)_i$ with probability $(\hat{\boldsymbol{p}}_n^N)_i$, so that

$$\langle X_n \rangle = h_n^N, \tag{3.83a}$$

$$\langle (X_n - \langle X_n \rangle)^2 \rangle = v_n^N, \tag{3.83b}$$

$$\langle |X_n - \langle X_n \rangle|^3 \rangle = y_n^N, \tag{3.83c}$$

where the average $\langle \cdot \rangle$ is taken with respect to the distribution $\hat{\boldsymbol{p}}_n^N$. We then have the following

$$\begin{aligned} &\sum_i \left\{ \hat{P}_i^N \middle| \hat{P}_i^N \geq \frac{1}{l(x)} \right\} \\ &= \sum_{i_1,\ldots,i_N} \left\{ \prod_{n=1}^N (\hat{\boldsymbol{p}}_n^N)_{i_n} \middle| \prod_{n=1}^N (\hat{\boldsymbol{p}}_n^N)_{i_n} \geq \frac{1}{l(x)} \right\} \\ &= \sum_{i_1,\ldots,i_N} \left\{ \prod_{n=1}^N (\hat{\boldsymbol{p}}_n^N)_{i_n} \middle| -\sum_{n=1}^N \log(\hat{\boldsymbol{p}}_n^N)_{i_n} \leq \log l(x) \right\} \\ &= \Pr\left[\sum_{n=1}^N X_n \leq N h_N + x\sqrt{N v_N} \right] \\ &= \Pr\left[\frac{\sum_{n=1}^N (X_n - \langle X_n \rangle)}{\sqrt{\sum_{n=1}^N \langle (X_n - \langle X_n \rangle)^2 \rangle}} \leq x \right]. \end{aligned} \tag{3.84}$$

Now, the Berry-Esseen theorem [120, 121] tells us that

$$\left|\Pr\left[\frac{\sum_{n=1}^{N}(X_n-\langle X_n\rangle)}{\sqrt{\sum_{n=1}^{N}\langle(X_n-\langle X_n\rangle)^2\rangle}}\leq x\right]-\Phi(x)\right|\leq\frac{Cy_N}{\sqrt{Nv_N^3}},\tag{3.85}$$

where C is a constant that was bounded in Refs. [122, 123] by

$$0.4097\leq C\leq 0.4748.\tag{3.86}$$

We thus have

$$\left|\sum_i\left\{\hat{P}_i^N\middle|\hat{P}_i^N\geq\frac{1}{l(x)}\right\}-\Phi(x)\right|\leq\frac{Cy_N}{\sqrt{Nv_N^3}},\tag{3.87}$$

and so we infer that the error ϵ_N is bounded from above by

$$\epsilon_N\leq\Phi\left(-\frac{\Delta F^N}{\sigma(F^N)}\right)+\frac{C\kappa^3(F^N)}{\sigma^3(F^N)},\tag{3.88}$$

that proves the single-shot upper bound on transformation error, Eq. (3.26), presented in theorem 26A. Also, one should note from Eq. (3.88), that if $\lim_{N\to\infty}v_n$ and $\lim_{N\to\infty}y_n$ are well-defined and non-zero (which is our assumption), then

$$\lim_{N\to\infty}\epsilon_N\leq\lim_{N\to\infty}\Phi\left(-\frac{\Delta F^N}{\sigma(F^N)}\right).\tag{3.89}$$

3.5.2.2 Lower bound for the transformation error

In order to lower bound the expression for the optimal error in the asymptotic limit, we choose $\alpha=\exp(\delta\sqrt{N})$ with $\delta>0$ in Eq. (3.69b). Therefore, from Eq. (3.71) and Eq. (3.76) we can write

$$l(x)\leq\frac{\chi_{\hat{\boldsymbol{P}}^N}(e^{\delta\sqrt{N}}l(x))}{c}=\frac{\chi_{\hat{\boldsymbol{P}}^N}(l(x+\delta))}{c},\tag{3.90}$$

where one can calculate c from Eq. (3.70):

$$\begin{aligned}c&=e^{\frac{\delta\sqrt{N}}{2}}\sum_{i=\chi_{\hat{\boldsymbol{P}}^N}(l(x+\delta/2))}^{\chi_{\hat{\boldsymbol{P}}^N}(l(x+\delta))}(\hat{\boldsymbol{P}}^N)_i^{\downarrow}\\&=e^{\frac{\delta\sqrt{N}}{2}}\left(\sum_i\left\{\hat{P}_i^N\middle|\hat{P}_i^N\geq\frac{1}{l(x+\delta)}\right\}\right.\\&\qquad\left.-\sum_i\left\{\hat{P}_i^N\middle|\hat{P}_i^N\geq\frac{1}{l(x+\delta/2)}\right\}\right).\end{aligned}\tag{3.91}$$

Employing Eq. (3.87) one can lower bound the above expression as

$$c \geq e^{\frac{\delta\sqrt{N}}{2}} \left(\Phi(x+\delta) - \Phi(x+\delta/2) - \frac{2Cy_N}{\sqrt{Nv_N^3}} \right). \tag{3.92}$$

Now, for any finite $\delta > 0$, it is clear that there exists N_0 such that for all $N \geq N_0$ we have $c > 1$. Combining with Eq. (3.90), for large enough N we finally have

$$l(x) \leq \frac{\chi_{\hat{\boldsymbol{P}}^N}(l(x+\delta))}{c} \leq \chi_{\hat{\boldsymbol{P}}^N}(l(x+\delta)). \tag{3.93}$$

Hence, using Eq. (3.93), we have the following lower bound on transformation error

$$\begin{aligned} \epsilon_N = 1 - \sum_{i=1}^{l(x)} (\hat{\boldsymbol{P}}^N)_i^{\downarrow} &\geq 1 - \sum_{i=1}^{\chi_{\hat{\boldsymbol{P}}^N}(l(x+\delta))} (\hat{\boldsymbol{P}}^N)_i^{\downarrow} \\ &= 1 - \sum_i \left\{ \hat{P}_i^N \middle| \hat{P}_i^N \geq \frac{1}{l(x+\delta)} \right\} \\ &\geq 1 - \Phi(x+\delta) - \frac{Cy_N}{\sqrt{Nv_N^3}}, \end{aligned} \tag{3.94}$$

where in the last line we used Eq. (3.87) again. It is thus clear that

$$\lim_{N\to\infty} \epsilon_N \geq 1 - \lim_{N\to\infty} \Phi(x+\delta) = \lim_{N\to\infty} \Phi(-x-\delta) \tag{3.95}$$

and, since it works for any $\delta > 0$, we conclude that

$$\lim_{N\to\infty} \epsilon_N \geq \lim_{N\to\infty} \Phi\left(-\frac{\Delta F^N}{\sigma(F^N)} \right). \tag{3.96}$$

Combining the above with the bound obtained in Eq. (3.89), we finally get

$$\lim_{N\to\infty} \epsilon_N = \lim_{N\to\infty} \Phi\left(-\frac{\Delta F^N}{\sigma(F^N)} \right), \tag{3.97}$$

which proves the asymptotic expression for the transformation error, Eq. (3.25), presented in theorem 26A.

3.5.3 Proof of theorem 26B

To prove theorem 26B, we will break it down into two parts. Initially, we will determine the embedded version of the optimal final state, which minimizes the dissipation of free energy F_{diss}^N. We will then derive the expression for F_{diss}^N as a function of the initial state. Subsequently, we will calculate F_{diss}^N up to the second-order asymptotic terms. We will accomplish this by both upper and lower bounding the expression and showing that the bounds coincide.

3.5.3.1 Deriving optimal dissipation

We begin by presenting an extension of lemma 29 that not only yields the optimal transformation error for approximate majorisation but also leads to the optimal final state.

Lemma 31. *Let $\boldsymbol{p}$ and $\boldsymbol{q}$ be classical state of size d with $V(\boldsymbol{q}) = 0$ and $H(\boldsymbol{q}) = \log L$. Then, states $\boldsymbol{r}$ saturating $\boldsymbol{p} \succ_\epsilon \boldsymbol{q}$, i.e., such that $\boldsymbol{p} \succ \boldsymbol{r}$ and $F(\boldsymbol{q}, \boldsymbol{r}) = 1 - \epsilon$ with ϵ being the minimal value specified by lemma 29, are given by $\Pi \boldsymbol{q}^*$, where Π is an arbitrary permutation,*

$$\boldsymbol{q}^* \quad := \quad \begin{cases} \frac{1-\epsilon}{L} & \text{for } i \leq L, \\ B\boldsymbol{p}'_{i-L} & \text{for } i > L, \end{cases} \tag{3.98}$$

where B is an arbitrary $(d-L) \times (d-L)$ bistochastic matrix, and $\boldsymbol{p}'$ is a classical state of size $(d-L)$ with $p'_i = p^{\downarrow}_{i+L}$. Moreover, among all such distributions $\Pi \boldsymbol{q}^*$, the entropy is minimised for the one with B is the identity matrix.

The proof for the lemma mentioned above can be found in appendix 6.3. Here we use it to analyze the central Eq.(3.58), that outlines the necessary conditions for the ϵ-approximate thermodynamic distillation process being investigated. This results in the actual total final state in the embedded picture, $\hat{\boldsymbol{F}}^N$, which is ϵ distance away from the target state $\hat{\boldsymbol{G}}^N \otimes \tilde{\boldsymbol{f}}_k^N$, as given below (up to permutations):

$$\hat{\boldsymbol{F}}^N \quad = \quad \begin{cases} \frac{1-\epsilon}{K} & \text{for } i \leq K, \\ (\hat{\boldsymbol{P}}^N \otimes \tilde{\boldsymbol{\eta}}^N)^{\downarrow}_i & \text{for } i > K, \end{cases}, \tag{3.99}$$

where

$$K = \exp(H(\hat{\boldsymbol{G}}^N) + H(\tilde{\boldsymbol{f}}_k^N)). \tag{3.100}$$

Observe that we have chosen $\hat{\boldsymbol{F}}^N$ to minimise entropy since, due to Eq. (3.60a), as it translates into the real (unembedded) final state $\boldsymbol{F}^N$ with maximal free energy, i.e., it leads to minimal free energy dissipation.

The next step involves moving back to the unembedded picture from the embedded oneone. It's worth noting that if a state within the embedded representation is non-uniform within each embedding box, then unembedding will result in a loss of free energy. However, we can rearrange the elements of the final state given by Eq. (3.99) to minimize this loss, as the equation is only valid up to permutations. In appendix 6.6, we show that a permutation exists that transforms $\hat{\boldsymbol{F}}^N$ into a state that is uniform within almost all embedding boxes, leading to exponentially small dissipation of free energy (i.e., no dissipation up to second-order asymptotics) for the case of identical initial states (i.e., $\boldsymbol{P}^N = \boldsymbol{p}^{\otimes N}$). Therefore, employing the definition of dissipated free energy from Eq. (3.24) and the above discussion, we have

$$\begin{aligned}F_{\text{diss}}^{N} =&\frac{1}{\beta}\left(D(\boldsymbol{P}^{N}\|\boldsymbol{G}^{N}) - D(\boldsymbol{F}^{N}\|\boldsymbol{G}^{N}\otimes\tilde{\boldsymbol{G}}^{N})\right)\\ \simeq&\frac{1}{\beta}\left(H(\hat{\boldsymbol{F}}^{N}) - H(\hat{\boldsymbol{P}}^{N}) - \log\tilde{D}\right). \end{aligned} \tag{3.101}$$

Here, $\tilde{D}$ is the embedding constant as defined by $\tilde{\boldsymbol{G}}^{N}$ in Eq. (3.52). Similarly, we will use D to denote the embedding constant for $\boldsymbol{G}^{N}$. It is worth noting, however, that these constants can be selected to be equal since what is important is that $\tilde{G}_{k}^{N} = \tilde{D}_{k}/\tilde{D}$ and $G_{k}^{N} = D_{k}/D$. In other words, any changes to $\tilde{D}$ or D can be counterbalanced by a corresponding modification to $\tilde{D}_{k}$ or D_{k}.

Next, noting that $K = D\tilde{D}_{k} = \tilde{D}\tilde{D}_{k}$, one can calculate the entropy of $\hat{\boldsymbol{F}}^{N}$:

$$\begin{aligned}H(\hat{\boldsymbol{F}}^{N}) =& -\sum_{i=1}^{K}\frac{1-\epsilon}{K}\log\left(\frac{1-\epsilon}{K}\right) - \sum_{i>\tilde{D}_{k}}(\hat{\boldsymbol{P}}^{N})_{i}^{\downarrow}\log\frac{(\hat{\boldsymbol{P}}^{N})_{i}^{\downarrow}}{\tilde{D}}\\ =& -(1-\epsilon)\log(1-\epsilon) + (1-\epsilon)\log K - \sum_{i>\tilde{D}_{k}}(\hat{\boldsymbol{P}}^{N})_{i}^{\downarrow}\log(\hat{\boldsymbol{P}}^{N})_{i}^{\downarrow} + \epsilon\log\tilde{D}\\ \simeq&\log\tilde{D} + (1-\epsilon)\log\tilde{D}_{k} - \sum_{i>\tilde{D}_{k}}(\hat{\boldsymbol{P}}^{N})_{i}^{\downarrow}\log(\hat{\boldsymbol{P}}^{N})_{i}^{\downarrow}, \end{aligned} \tag{3.102}$$

where we have dropped the term $(1-\epsilon)\log(1-\epsilon)$ since it is constant (i.e. it does not scale with N). Hence, the amount of dissipated free energy in the optimal distillation process is simply calculated as

$$F_{\text{diss}}^{N} \simeq \frac{1}{\beta}\left((1-\epsilon)\log\tilde{D}_{k} + \sum_{i=1}^{\tilde{D}_{k}}(\hat{\boldsymbol{P}}^{N})_{i}^{\downarrow}\log(\hat{\boldsymbol{P}}^{N})_{i}^{\downarrow}\right). \tag{3.103}$$

3.5.3.2 Calculating optimal dissipation

We now proceed to prove the bounds for F_{diss}^{N}. To do so, we first make use of Eq. (3.71) and the fact that $\log x$ is negative for all $x \in (0,1)$ to write

$$\sum_{i=1}^{\tilde{D}_{k}}(\hat{\boldsymbol{P}}^{N})_{i}^{\downarrow}\log(\hat{\boldsymbol{P}}^{N})_{i}^{\downarrow} \leq \sum_{i=1}^{\chi_{\hat{\boldsymbol{P}}^{N}}(\tilde{D}_{k})}(\hat{\boldsymbol{P}}^{N})_{i}^{\downarrow}\log(\hat{\boldsymbol{P}}^{N})_{i}^{\downarrow}. \tag{3.104}$$

The right-hand side of the above can then be expressed as follows,

$$\begin{aligned}
\sum_{i=1}^{\chi_{\hat{\boldsymbol{P}}^N}(\tilde{D}_k)} (\hat{\boldsymbol{P}}^N)_i^{\downarrow} \log(\hat{\boldsymbol{P}}^N)_i^{\downarrow} &= \sum_i \left\{ \hat{P}_i^N \log(\hat{P}_i^N) \middle| \hat{P}_i^N \geq \frac{1}{\tilde{D}_k} \right\} \\
&= \sum_{i_1,\dots,i_N} \left\{ \prod_{n=1}^{N} (\hat{\boldsymbol{p}}_n^N)_{i_n} \sum_{m=1}^{N} \log(\hat{\boldsymbol{p}}_m^N)_{i_m} \middle| \prod_{n=1}^{N} (\hat{\boldsymbol{p}}_n^N)_{i_n} \geq \frac{1}{\tilde{D}_k} \right\} \\
&= \sum_{i_1,\dots,i_N} \left\{ \prod_{n=1}^{N} (\hat{\boldsymbol{p}}_n^N)_{i_n} \sum_{m=1}^{N} \log(\hat{\boldsymbol{p}}_m^N)_{i_m} \middle| -\sum_{m=1}^{N} \log(\hat{\boldsymbol{p}}_m^N)_{i_m} \leq \log \tilde{D}_k \right\}. \qquad (3.105)
\end{aligned}$$

Note that from the definition in Eq. (3.23) we have (here we employ the notation introduced in Eqs. (3.75a)-(3.75c)):

$$\begin{aligned}
\beta \Delta F^N &= \sum_{n=1}^{N} D(\boldsymbol{p}_n^N \| \boldsymbol{\gamma}_n^N) - D(\tilde{\boldsymbol{s}}_k^N \| \tilde{\boldsymbol{\gamma}}^N) \\
&= H(\tilde{\boldsymbol{f}}_k^N) - \sum_{n=1}^{N} H(\hat{\boldsymbol{p}}_n^N) = \log \tilde{D}_k - N h_N. \qquad (3.106)
\end{aligned}$$

Next, since for a non-trivial error we require

$$\beta \Delta F^N = x \beta \sigma(F^N) = x\sqrt{N v_N}, \qquad (3.107)$$

with some constant x, we can rewrite $\log \tilde{D}_k$ as

$$\log \tilde{D}_k = N h_N + x\sqrt{N v_N}. \qquad (3.108)$$

Returning back to Eq. (3.105), one can express it by introducing N discrete random variables $\{X_n\}_{n=1}^N$ assuming values $-\log(\hat{\boldsymbol{p}}_n^N)_{i_n}$ with probability $(\hat{\boldsymbol{p}}_n^N)_{i_n}$. Importantly, since the sum of their averages is $N h_N$ and their total variance is $N v_N$, the condition in the summation in Eq. (3.105) simply reduces to:

$$Y_N := \frac{\sum_{n=1}^{N} (X_n - \langle X_n \rangle)}{\sqrt{\sum_{n=1}^{N} \langle (X_n - \langle X_n \rangle)^2 \rangle}} \leq x. \qquad (3.109)$$

Thus, we can write Eq. (3.105) in a compact way as follows

$$\sum_{i=1}^{\chi_{\hat{\boldsymbol{P}}^N}(\tilde{D}_k)} (\hat{\boldsymbol{P}}^N)_i^{\downarrow} \log(\hat{\boldsymbol{P}}^N)_i^{\downarrow} = -\int_T \sum_{n=1}^{N} X_N dP, \qquad (3.110)$$

where P is discrete probability measure given by $P(i_1, \dots, i_N) = \prod_{n=1}^{N} (\hat{\boldsymbol{p}}_n^N)_{i_n}$ and T is a region satisfying the constraint $Y_N < x$. Observing that

$$\sum_{n=1}^{N} X_n = \sqrt{N v_n} Y_N + N h_N \tag{3.111}$$

we can further rewrite it as

$$\int_T \sum_{n=1}^{N} X_N dP = \sqrt{N v_N} \int_{Y_N \leq x} Y_N dP + N h_N \int_{Y_N \leq x} dP. \tag{3.112}$$

The second integral on the right-hand side of the above was already calculated and is equal to $1-\epsilon$, where ϵ is the optimal transformation error from theorem 26A. In addition, since Y_N is a standarized sum of independent random variables, its distribution approaches to a normal Gaussian distribution with density denoted by $\phi(x)$, i.e.,

$$\int_{Y_N \leq x} Y_N dP \simeq \int_{-\infty}^{x} y\phi(y)dy = -\frac{e^{-x^2/2}}{\sqrt{2\pi}}. \tag{3.113}$$

Therefore, we get:

$$\begin{aligned}
\sum_{i=1}^{\chi_{\hat{\boldsymbol{P}}^N}(\tilde{D}_k)} (\hat{\boldsymbol{P}}^N)_i^{\downarrow} \log(\hat{\boldsymbol{P}}^N)_i^{\downarrow} &\simeq \sqrt{N v_N} \frac{e^{-x^2/2}}{\sqrt{2\pi}} - N h_N (1-\epsilon) \\
&= \sqrt{N v_N} \frac{e^{-x^2/2}}{\sqrt{2\pi}} - (1-\epsilon)(\log \tilde{D}_k - x\sqrt{N v_N}) \\
&= \beta\sigma(F^N)\left(\frac{e^{-x^2/2}}{\sqrt{2\pi}} + x(1-\epsilon)\right) - (1-\epsilon)\log \tilde{D}_k. \qquad (3.114)
\end{aligned}$$

Now we shall employ the inequality from Eq. (3.104) and substitute the above to Eq. (3.103) to obtain:

$$F_{\text{diss}}^N \lesssim \sigma(F^N)\left(\frac{e^{-x^2/2}}{\sqrt{2\pi}} + x(1-\epsilon)\right). \tag{3.115}$$

Next, using Eq. (3.107) and the expression for optimal transformation error from Theorem 26A, we can re-express x as

$$x = -\Phi^{-1}(\epsilon) \tag{3.116}$$

to finally obtain

$$F_{\text{diss}}^N \lesssim \sigma(F^N)\left(\frac{e^{\frac{-(\Phi^{-1}(\epsilon))^2}{2}}}{\sqrt{2\pi}} - \Phi^{-1}(\epsilon)(1-\epsilon)\right). \tag{3.117}$$

In order to provide a lower bound of F_{diss}^N given in Eq. (3.103), we simply follow the argument we have provided in section 3.5.2.2. From Eq. (3.69b) it easily follows that

$$\sum_{i=1}^{\tilde{D}_k} (\hat{\boldsymbol{P}}^N)_i^{\downarrow} \log(\hat{\boldsymbol{P}}^N)_i^{\downarrow} \geq \sum_{i=1}^{\frac{\chi_{\hat{\boldsymbol{P}}^N}(\tilde{D}_k e^{\delta\sqrt{N}})}{c}} (\hat{\boldsymbol{P}}^N)_i^{\downarrow} \log(\hat{\boldsymbol{P}}^N)_i^{\downarrow}, \tag{3.118}$$

where c, as before, can be lower bounded by 1 for large enough N. Hence we obtain

$$F_{\text{diss}}^N \gtrsim \frac{1}{\beta}\left((1-\epsilon)\log\tilde{D}_k + \sum_{i=1}^{\chi_{\hat{\boldsymbol{P}}^N}(\tilde{D}_k e^{\delta\sqrt{N}})} (\hat{\boldsymbol{P}}^N)_i^{\downarrow} \log(\hat{\boldsymbol{P}}^N)_i^{\downarrow}\right). \tag{3.119}$$

Since the above inequality satisfies for any $\delta > 0$, therefore the limit $\delta \to 0$ we get

$$F_{\text{diss}}^N \gtrsim \sigma(F^N)\left(\frac{e^{\frac{-(\Phi^{-1}(\epsilon))^2}{2}}}{\sqrt{2\pi}} - \Phi^{-1}(\epsilon)(1-\epsilon)\right). \tag{3.120}$$

Combining the above with the upper bound from Eq. (3.117), we finally obtain

$$F_{\text{diss}}^N \simeq a(\epsilon)\sigma(F^N), \tag{3.121}$$

where $a(\epsilon)$ is provided by Eq. (3.29).

3.5.4 Proof of theorem 27A

The proof of theorem 27A will be presented in three parts. Firstly, it will be demonstrated that a thermodynamic distillation procedure from a general state ρ can be reduced to a distillation process from an incoherent state that represents a dephased form of ρ. Using this observation, the problem under investigation will be reformulated in terms of approximate majorisation and thermomajorisation, as explained in section 3.5.1. The second part of the proof will derive the upper bound for the optimal transformation error ϵ_N. The third and final part will establish a lower bound for ϵ_N and demonstrate that it approaches the derived upper bound in the asymptotic limit. Thus, Eq. (3.32) will be proved.

3.5.4.1 Reducing the problem to the incoherent case

The problem being investigated is the thermodynamic distillation, which can be described as follows: the family initial systems comprises N indistinguishable subsystems, each with an equivalent Hamiltonian represented by

$$H = \sum_{i=1}^{d} E_i |E_i\rangle\langle E_i|, \tag{3.122}$$

along with an ancillary system having any Hamiltonian H_A. It should be noted that the dimension of the ancillary system can always be set to 1 to disregard it. The family of initial states is given by

$$\rho^N = \psi^{\otimes N} \otimes |E_0^A\rangle\langle E_0^A|, \tag{3.123}$$

where

$$\psi = |\psi\rangle\langle\psi|, \quad |\psi\rangle = \sum_{i=1}^{d} \sqrt{p_i} e^{i\phi_i} |E_i\rangle, \tag{3.124}$$

is an arbitrary pure state and $|E_0^A\rangle$ is an eigenstate of H_A with energy E_0^A. The family of target systems is composed of subsystems described by arbitrary Hamiltonians $\tilde{H}^N$ and a subsystem described by the Hamiltonian H_A. The set of target states is defined as follows:

$$\tilde{\rho}^N = |\tilde{E}_k^N\rangle\langle\tilde{E}_k^N| \otimes |E_1^A\rangle\langle E_1^A|, \tag{3.125}$$

where $|\tilde{E}_k^N\rangle$ denotes an eigenstate of $\tilde{H}^N$, and $|E_1^A\rangle$ is an eigenstate of H_A having an energy of E_1^A. We are interested to explore a thermal operation $\mathcal{E}$ that can approximately accomplish the following transformation:

$$\psi^{\otimes N} \otimes |E_0^A\rangle\langle E_0^A| \xrightarrow{\mathcal{E}} |\tilde{E}_k^N\rangle\langle\tilde{E}_k^N| \otimes |E_1^A\rangle\langle E_1^A|. \tag{3.126}$$

We now have the following simple, but very useful, lemma.

Lemma 32. *If an incoherent state σ achievable from a state ρ via a thermal operation, then it is also achievable from $\mathcal{D}(\rho)$, where $\mathcal{D}$ is the dephasing operation that destroys the coherence between different energy subspaces:*

$$\exists\mathcal{E} : \mathcal{E}(\rho) = \sigma \quad \Leftrightarrow \quad \mathcal{E}(\mathcal{D}(\rho)) = \sigma. \tag{3.127}$$

Proof. Let us consider a general state ρ and an incoherent state σ. Suppose that there exists a thermal operation $\mathcal{E}$ such that $\mathcal{E}(\rho) = \sigma$. Using the result from proposition 26, which states that every thermal operation is covariant with respect to dephasing [89], and the property of incoherent σ invariant under dephasing i.e., $\mathcal{D}(\sigma) = \sigma$, we can obtain the following:

$$\mathcal{E}(\mathcal{D}(\rho)) = \mathcal{D}(\mathcal{E}(\rho)) = \mathcal{D}(\sigma) = \sigma. \tag{3.128}$$

Conversely, we note that the dephasing operation is itself a thermal operation, and thus the reverse implication also holds. □

Since the target state in our case is energy incoherent, we can employ the above result in order to restate our problem as the existence of a thermal operation $\mathcal{E}$ approximately performing the following transformation

$$\mathcal{D}(\psi^{\otimes N} \otimes |E_0^A\rangle\langle E_0^A|) \xrightarrow{\mathcal{E}} |\tilde{E}_{\boldsymbol{k}}^N\rangle\langle \tilde{E}_{\boldsymbol{k}}^N| \otimes |E_1^A\rangle\langle E_1^A|. \tag{3.129}$$

Since

$$\mathcal{D}(\psi^{\otimes N} \otimes |E_0^A\rangle\langle E_0^A|) = \mathcal{D}(\psi^{\otimes N}) \otimes |E_0^A\rangle\langle E_0^A|, \tag{3.130}$$

our problem further boils down to understanding the structure of the incoherent state $\mathcal{D}(\psi^{\otimes N})$. The state $\mathcal{D}(\psi^{\otimes N})$ is block diagonal in the energy eigenbasis and further can be diagonalized using rotations in a fixed energy subspace. Note that rotations in a fixed energy subspace considered to be free operations or thermal operations. After applying this procedure, an incoherent state is obtained, which is described by the probability vector $\boldsymbol{P}^N$ over the multi-index set $\boldsymbol{k}$. The vector $\boldsymbol{P}^N$ is given by the following equation:

$$P_{\boldsymbol{k}}^N = \binom{N}{k_1, ..., k_d} \prod_{i=1}^{d} p_i^{k_i}, \tag{3.131}$$

where d is the dimension of the Hilbert space, and p_i is the probability of the energy eigenstate i. It is worth noting that $P_{\boldsymbol{k}}^N$ specifies the probability of having k_1 systems in energy state E_1, k_2 systems in energy state E_2, and so on. Moreover, we assume that energy levels are incommensurable, ensuring that each vector $\boldsymbol{k}$ corresponds to a different total energy value.

We can simplify the problem of thermodynamic distillation from pure states by reducing it to thermodynamic distillation from incoherent states. Specifically, we use $\boldsymbol{s}_i^A$ and $\boldsymbol{f}_i^A$ to represent the sharp distributions corresponding to $|E_i^A\rangle$ and the corresponding flat states after embedding, respectively. Likewise, we use $\tilde{\boldsymbol{s}}_k^N$ and $\tilde{\boldsymbol{f}}_k^N$ to denote distributions related to the sharp state $|\tilde{E}_k^N\rangle$ and its corresponding flat state. The embedded Gibbs state for H^N, denoted as $\hat{\boldsymbol{G}}^N$, has a more simpler form than in Eq. (3.57) because all the initial systems have identical Hamiltonians. Similarly, $\hat{\boldsymbol{P}}^N$ represents the embedded initial state, and can be expressed as:

$$\hat{P}_{\boldsymbol{k},g_{\boldsymbol{k}}}^N = \binom{N}{k_1, ..., k_d} \prod_{i=1}^{d} \frac{p_i^{k_i}}{D_i^{k_i}}, \tag{3.132}$$

where $\gamma_i = D_i/D$ and $g_{\boldsymbol{k}}$ is an index for the degeneracy resulting from embedding. With this notation, we can express the distillation problem as:

$$\hat{\boldsymbol{P}}^N \otimes \boldsymbol{f}_0^A \otimes \tilde{\boldsymbol{\eta}} \succ_\epsilon \hat{\boldsymbol{G}}^N \otimes \boldsymbol{f}_1^A \otimes \tilde{\boldsymbol{f}}_k. \tag{3.133}$$

3.5.4.2 Upper bound for the transformation error

We start by noting that our target probability vector in Eq. (3.133) is flat, and so $V(\hat{\boldsymbol{G}}^N \otimes \boldsymbol{f}_1^A \otimes \tilde{\boldsymbol{f}}_k) = 0$. Hence, we can use lemma 29 and Eq. (3.65) to obtain the following relation for the optimal transformation error:

$$\epsilon_N = 1 - \sum_{j=1}^{L} (\hat{\boldsymbol{P}}^N)_j^{\downarrow} \tag{3.134}$$

where L is given by

$$\begin{aligned} L &= \exp[H(\hat{\boldsymbol{G}}^N) + H(\boldsymbol{f}_1^A) + H(\tilde{\boldsymbol{f}}_k) - H(\boldsymbol{f}_0^A) - H(\tilde{\boldsymbol{\eta}})] \\ &= \exp[H(\hat{\boldsymbol{G}}^N) - D(\tilde{\boldsymbol{f}}_k \| \tilde{\boldsymbol{\eta}}) - \beta(E_1^A - E_0^A)]. \end{aligned} \tag{3.135}$$

Note that in the present case ΔF^N, defined in Eq. (3.23), can be expressed as

$$\begin{aligned} \Delta F^N =& \frac{1}{\beta}\Big(D(\psi^{\otimes N}\|\gamma^{\otimes N}) + D(|E_0^A\rangle\langle E_0^A|\|\gamma_A) - D(|\tilde{E}_k^N\rangle\langle \tilde{E}_k^N|\|\tilde{\gamma}) - D(|E_1^A\rangle\langle E_1^A|\|\gamma_A)\Big) \\ =& \frac{1}{\beta}\Big(ND(\psi\|\gamma) - D(\tilde{\boldsymbol{f}}_k\|\tilde{\boldsymbol{\eta}}) - \beta(E_1^A - E_0^A)\Big). \end{aligned} \tag{3.136}$$

Employing the above we can then rewrite L as

$$\log L = \beta \Delta F^N + H(\hat{\boldsymbol{G}}^N) - ND(\psi\|\gamma). \tag{3.137}$$

Now, using Eq. (3.69a) and Eq. (3.137), we set the upper bound for ϵ_N:

$$\begin{aligned} \epsilon_N &\leq 1 - \sum_{\boldsymbol{k},g_{\boldsymbol{k}}} \left\{ \hat{P}^N_{\boldsymbol{k},g_{\boldsymbol{k}}} \middle| \hat{P}^N_{\boldsymbol{k},g_{\boldsymbol{k}}} \geq \frac{1}{L} \right\} = 1 - \sum_{\boldsymbol{k}} \left\{ P^N_{\boldsymbol{k}} \middle| P^N_{\boldsymbol{k}} \geq \frac{\prod_{i=1}^d D_i^{k_i}}{L} \right\} \\ &= 1 - \sum_{\boldsymbol{k}} \left\{ P^N_{\boldsymbol{k}} \middle| \log P^N_{\boldsymbol{k}} \geq \sum_{i=1}^d k_i \log D_i - \log L \right\} \\ &= 1 - \sum_{\boldsymbol{k}} \left\{ P^N_{\boldsymbol{k}} \middle| \frac{\log P^N_{\boldsymbol{k}}}{N} \geq \sum_{i=1}^d \frac{k_i}{N} \log \gamma_i + D(\psi\|\gamma) - \frac{\beta}{N}\Delta F^N \right\}. \end{aligned} \tag{3.138}$$

To simplify the calculation of the upper bound of ϵ_N, one can rewrite each $\boldsymbol{k}$ as a function of a vector $\boldsymbol{s}$ such that

$$\boldsymbol{k} = \boldsymbol{k}(\boldsymbol{s}) = N\boldsymbol{p} + \sqrt{N}\boldsymbol{s}, \tag{3.139}$$

with $\sum_{i=1}^d s_i = 0$. We then observe that

$$D(\psi\|\gamma) = -\sum_{i=1}^d p_i \log \gamma_i, \tag{3.140}$$

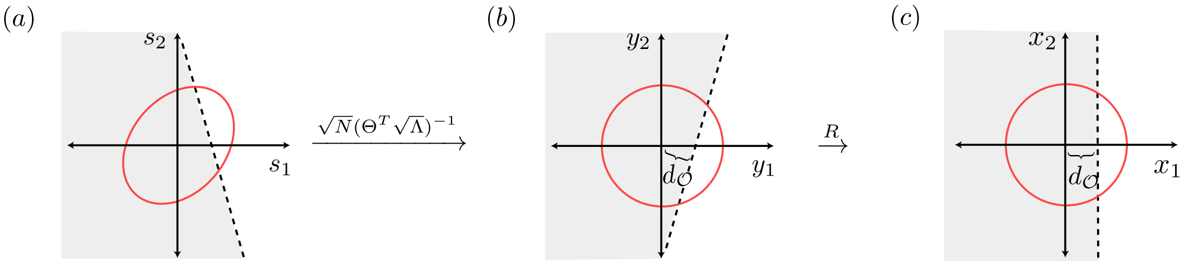

Figure 3.8: **Standardising the bivariate normal distribution**. The bivariate normal distribution with equal probability density points is depicted by a red ellipse centered at the origin, while the constraining hyperplane is represented by a black dashed line. The maximum value of ϵ_N is determined by the probability mass within the shaded area. To compute this value, we first perform a rotation and scaling transformation that makes the ellipse symmetric with respect to the origin. Then, by utilizing the rotational symmetry of the standard bivariate normal distribution, we can rotate the ellipse such that the hyperplane becomes parallel to the x_2 axis.

and thus the condition in Eq. (3.138) can be expressed as

$$\frac{\log P^N_{\boldsymbol{k}(\boldsymbol{s})}}{N} \geq \frac{1}{\sqrt{N}}\sum_{i=1}^{d} s_i \log\gamma_i - \frac{\beta}{N}\Delta F^N = -\frac{\beta}{\sqrt{N}}\sum_{i=1}^{d} s_i E_i - \frac{\beta}{N}\Delta F^N. \tag{3.141}$$

As we shall rigorously prove in appendix 6.4, the left-hand side of the above vanishes much faster than the right-hand side when $N \to \infty$, leading to

$$\lim_{N\to\infty} \epsilon_N \leq 1 - \lim_{N\to\infty} \sum_{\boldsymbol{s}} \left\{ P^N_{\boldsymbol{k}(\boldsymbol{s})} \middle| \sum_{i=1}^{d} s_i E_i \geq -\frac{\Delta F^N}{\sqrt{N}} \right\}. \tag{3.142}$$

The aim is then to calculate the sum of $P^N_{\boldsymbol{k}(\boldsymbol{s})}$ in the limit $N \to \infty$ constrained by the following hyperplane

$$\boldsymbol{s}\cdot\boldsymbol{E} \geq -\frac{\Delta F^N}{\sqrt{N}}, \tag{3.143}$$

where $\boldsymbol{E}$ is a vector of energies (spectrum of the Hamiltonian H). To do so, we start by approximating the multinomial distribution $\boldsymbol{P}^N$ specified in Eq. (3.131) by a multivariate normal distribution $\mathcal{N}^{(\boldsymbol{\mu},\boldsymbol{\Sigma})}$ with mean vector $\boldsymbol{\mu} = N\boldsymbol{p}$ and covariance matrix $\boldsymbol{\Sigma} = N(\operatorname{diag}(\boldsymbol{p}) - \boldsymbol{p}\boldsymbol{p}^T)$:

$$\begin{aligned} \mathcal{N}^{(\boldsymbol{\mu},\boldsymbol{\Sigma})}_{\boldsymbol{k}(\boldsymbol{s})} &= \frac{1}{\sqrt{(2\pi)^d|\boldsymbol{\Sigma}|}} \exp\left(-\frac{1}{2}(\boldsymbol{k}-\boldsymbol{\mu})^T\boldsymbol{\Sigma}^{-1}(\boldsymbol{k}-\boldsymbol{\mu})\right) \\ &= \frac{1}{\sqrt{(2\pi)^d|\boldsymbol{\Sigma}|}} \exp\left(-\frac{1}{2}\boldsymbol{s}^T N\boldsymbol{\Sigma}^{-1}\boldsymbol{s}\right). \end{aligned} \tag{3.144}$$

As we shall show in appendix 6.5, one can always do such an approximation with an error approaching 0 as $N \to \infty$. To proceed further, we standardise the multivariate normal distribution $\mathcal{N}^{(\boldsymbol{\mu},\boldsymbol{\Sigma})}$ using rotation and scaling transformations:

$$\boldsymbol{\Sigma} = \Theta^T \sqrt{\boldsymbol{\Lambda}} \sqrt{\boldsymbol{\Lambda}} \Theta, \tag{3.145}$$

where $\boldsymbol{\Lambda}$ is a diagonal matrix with the eigenvalues of $\boldsymbol{\Sigma}$ and Θ is an orthogonal matrix with columns given by the eigenvectors of $\boldsymbol{\Sigma}$. We depicted this process for a qutrit system (so described by s_1 and s_2 since $\sum_i s_i = 0$) in Fig. 3.8. This rotation and scaling of co-ordinates allows us to write $\mathcal{N}^{(\boldsymbol{\mu},\boldsymbol{\Sigma})}$ as a product of univariate standard normal distribution $\phi(y_i)$:

$$\mathcal{N}^{(\boldsymbol{\mu},\boldsymbol{\Sigma})}_{\boldsymbol{k}(\boldsymbol{s}(\boldsymbol{y}))} = \frac{1}{\sqrt{(2\pi)^d |\boldsymbol{\Sigma}|}} \exp\left(-\frac{1}{2}\boldsymbol{y}^T \boldsymbol{y}\right) = \prod_{i=1}^{d} \phi(y_i), \tag{3.146}$$

where

$$\boldsymbol{y} = \sqrt{N}(\Theta^T \sqrt{\boldsymbol{\Lambda}})^{-1} \boldsymbol{s}. \tag{3.147}$$

Then, one can equivalently rewrite the equation specifying the hyperplane, Eq. (3.143), as

$$(\Theta^T \sqrt{\boldsymbol{\Lambda}} \boldsymbol{y}) \cdot \boldsymbol{E} \geq -\Delta F^N. \tag{3.148}$$

Note that the standard normal distribution described in Eq. (3.146) maintains rotational invariance with respect to the origin. Consequently, we can choose a coordinate system $\boldsymbol{x} = x_1, \ldots, x_d$ by performing an appropriate rotation R on $\boldsymbol{y} = y_1, \ldots, y_d$ such that the hyperplane specified in Eq. (3.143) becomes parallel to all coordinate axes except for the x_1 axis. By doing so, we can express Eq. (3.146) in the following manner:

$$\mathcal{N}^{(\boldsymbol{\mu},\boldsymbol{\Sigma})}_{\boldsymbol{k}(\boldsymbol{s}(\boldsymbol{x}))} = \frac{1}{\sqrt{(2\pi)^d |\boldsymbol{\Sigma}|}} \exp\left(-\frac{1}{2}\boldsymbol{x}^T \boldsymbol{x}\right) = \prod_{i=1}^{d} \phi(x_i). \tag{3.149}$$

As we have

$$\boldsymbol{x} = R\boldsymbol{y}, \tag{3.150}$$

we can use it together with Eq. (3.147) to rewrite Eq. (3.143) as

$$\Theta^T \sqrt{\boldsymbol{\Lambda}} R^T \boldsymbol{x} \cdot \boldsymbol{E} \geq -\Delta F^N. \tag{3.151}$$

In order to determine the right-hand side of the inequality presented in Eq. (3.142) as N approaches infinity, we must integrate Eq. (3.149) over x_1 from negative infinity to $d_{\mathcal{O}}$, and over any other $x_i \neq x_1$ from negative infinity to positive infinity. Here, $d_{\mathcal{O}}$ represents the signed distance of the hyperplane specified in Eq. (3.151) from the origin, as illustrated in

Fig. 3.8. The value of $d_{\mathcal{O}}$ can be computed explicitly using the following expression:

$$d_{\mathcal{O}} = \frac{\Delta F^N}{\sqrt{\boldsymbol{E}\cdot(R\sqrt{\boldsymbol{\Lambda}}\Theta)^T(R\sqrt{\boldsymbol{\Lambda}}\Theta)\boldsymbol{E}}} = \frac{\Delta F^N}{\sqrt{\boldsymbol{E}\cdot(\boldsymbol{\Sigma}\boldsymbol{E})}} = \frac{\Delta F^N}{\sigma(F^N)}, \tag{3.152}$$

where $\sigma(F^N)$ is defined in Eq. (3.22b). Thus, the upper bound on ϵ_N in the limit as N approaches infinity, as given by Eq. (3.142), can be evaluated in the following manner:

$$\begin{aligned}&1-\lim_{N\to\infty}\int_{-\infty}^{+\infty}dx_d\phi(x_d)\ldots\int_{-\infty}^{+\infty}dx_2\phi(x_2)\int_{-\infty}^{d_{\mathcal{O}}}dx_1\phi(x_1)\\ &=1-\lim_{N\to\infty}\Phi(d_{\mathcal{O}})=\lim_{N\to\infty}\Phi\left(-\frac{\Delta F^N}{\sigma(F^N)}\right).\end{aligned} \tag{3.153}$$

3.5.4.3 Lower bound for the transformation error

We begin by writing L from Eq. (3.137) as

$$L=\exp\left(AN+x\sqrt{Nv_N}\right)=:L(x), \tag{3.154}$$

where

$$A=H(\boldsymbol{\eta})-D(\psi\|\gamma),\qquad x=\frac{\Delta F^N}{\sigma(F^N)}. \tag{3.155}$$

In the previous section, we exactly computed the right-hand side of Eq. (3.138) in the limit as N approaches to infinity, as shown in Eq. (3.153). By using equations (3.154)-(3.155), we can also express this result as

$$\lim_{N\to\infty}\sum_{\boldsymbol{k},g_{\boldsymbol{k}}}\left\{\hat{P}^N_{\boldsymbol{k},g_{\boldsymbol{k}}}\middle|\hat{P}^N_{\boldsymbol{k},g_{\boldsymbol{k}}}\geq\frac{1}{L(x)}\right\}=\lim_{N\to\infty}\Phi(x), \tag{3.156}$$

where x depends on N as described in Eq. (3.155). We will now use the exact expression from Eq. (3.134) and the inequality presented in Eq. (3.69b) to prove the lower bound for the transformation error ϵ_N. Similarly as before, we choose $\alpha=\exp(\delta\sqrt{N})$ in Eq. (3.69b), where $\delta>0$. Thus, employing Eq. (3.71) and Eq. (3.154), we have

$$L(x)\leq\frac{\chi_{\hat{\boldsymbol{P}}^N}(e^{\delta\sqrt{N}}L(x))}{c}=\frac{\chi_{\hat{\boldsymbol{P}}^N}(L(x+\delta))}{c}, \tag{3.157}$$

where c can be computed in a similar manner as before.

$$\begin{aligned}c &= e^{\delta\sqrt{N}/2} \sum_{i=\chi_{\hat{\boldsymbol{P}}^N}(e^{\delta\sqrt{N}/2}L(x))}^{\chi_{\hat{\boldsymbol{P}}^N}(e^{\delta\sqrt{N}}L(x))} (\hat{\boldsymbol{P}}^N)_i^{\downarrow} = e^{\delta\sqrt{N}/2} \sum_{i=\chi_{\hat{\boldsymbol{P}}^N}(L(x+\delta/2))}^{\chi_{\hat{\boldsymbol{P}}^N}(L(x+\delta))} (\hat{\boldsymbol{P}}^N)_i^{\downarrow} \\ &= e^{\delta\sqrt{N}/2} \left(\sum_i \left\{ \hat{P}_i^N \middle| \hat{P}_i^N \geq \frac{1}{L(x+\delta)} \right\} - \sum_i \left\{ \hat{P}_i^N \middle| \hat{P}_i^N \geq \frac{1}{L(x+\delta/2)} \right\} \right). \end{aligned} \tag{3.158}$$

Employing Eq. (3.156), we observe that the limiting behaviour of c from Eq. (3.158) can be written as

$$\lim_{N\to\infty} c = (\Phi(x+\delta) - \Phi(x+\delta/2)) \lim_{N\to\infty} e^{\delta\sqrt{N}/2}. \tag{3.159}$$

So, for any finite $\delta > 0$, there certainly exists N_0 such that for all $N \geq N_0$ we have $c > 1$. Combining with Eq. (3.157), for large enough N we finally obtain,

$$L(x) \leq \frac{\chi_{\hat{\boldsymbol{P}}^N}(L(x+\delta))}{c} \leq \chi_{\hat{\boldsymbol{P}}^N}(L(x+\delta)). \tag{3.160}$$

Hence, using Eq. (3.160), we establish the following lower bound on transformation error

$$\begin{aligned}\lim_{N\to\infty} \epsilon_N &\geq 1 - \lim_{N\to\infty} \sum_{i=1}^{\chi_{\hat{\boldsymbol{P}}^N}(L(x+\delta))} (\hat{\boldsymbol{P}}^N)_i^{\downarrow} = 1 - \lim_{N\to\infty} \sum_i \left\{ \hat{P}_i^N \middle| \hat{P}_i^N \geq \frac{1}{L(x+\delta)} \right\} \\ &= 1 - \lim_{N\to\infty} \Phi(x+\delta) = \lim_{N\to\infty} \Phi(-x-\delta), \end{aligned} \tag{3.161}$$

where the first equality in the last line follows from Eq. (3.156). As the above inequality is true for any $\delta > 0$, taking the limit $\delta \to 0$ we conclude that

$$\lim_{N\to\infty} \epsilon_N \geq \lim_{N\to\infty} \Phi\left(-\frac{\Delta F^N}{\sigma(F^N)}\right). \tag{3.162}$$

Combining the above with the bound obtain in Eq. (3.153), we finally conclude

$$\lim_{N\to\infty} \epsilon_N = \lim_{N\to\infty} \Phi\left(-\frac{\Delta F^N}{\sigma(F^N)}\right), \tag{3.163}$$

that completes the proof.

3.5.5 Proof of theorem 27B

We will prove theorem 27B by dividing it into two parts. First, we will identify the embedded version of the optimal final state that reduces the dissipation of free energy F_{diss}^N. Then, we will deduce the minimum value of F_{diss}^N as a function of the initial state. Finally, we will calculate this bound including second-order asymptotic terms.

3.5.5.1 Deriving bound for optimal dissipation

We begin by applying lemma 31 to the central Eq. (3.133) that specifies the conditions for the concerned ϵ-approximate thermodynamic distillation process. As a consequence, the actual embedded version of total final state is given by $\hat{\boldsymbol{F}}^N$, which is ϵ away from the target state $\hat{\boldsymbol{G}}^N \otimes \boldsymbol{f}_1^A \otimes \tilde{\boldsymbol{f}}_k$, is given, up to permutations, by

$$\hat{\boldsymbol{F}}^N = \begin{cases} \frac{1-\epsilon}{k} & \text{for } i \leq k, \\ (\hat{\boldsymbol{P}}^N \otimes \boldsymbol{f}_0^A \otimes \tilde{\boldsymbol{\eta}})_i^{\downarrow} & \text{for } i > k, \end{cases} \tag{3.164}$$

where

$$k = \exp\Big(H(\hat{\boldsymbol{G}}^N) + H(\boldsymbol{f}_1^A) + H(\tilde{\boldsymbol{f}}_k)\Big). \tag{3.165}$$

As previously, we chose $\hat{\boldsymbol{F}}^N$ with minimal entropy (i.e., we selected the bistochastic map B from Lemma 31 to be a permutation) to minimise the dissipation of free energy. Since the final state is only determined up to permutations, it's possible to rearrange its elements freely to lower the dissipation of free energy that arises due to unembedding (such dissipation happens when a state isn't uniform within every embedding box). However, unlike the previous scenario, this freedom of permutation doesn't always enable us to avoid additional dissipation. In the previous case, the number of non-uniform embedding boxes was exponentially small, that results a negligible loss of free energy due to unembedding. In contrast, the number of non-uniform embedding boxes isn't exponentially small in this scenario and could result a finite dissipation of free energy. Thus, in this case, we can only provide a lower bound on dissipation of free energy as follows:

$$\begin{aligned} F_{\text{diss}}^N =& \frac{1}{\beta}\Big(D(\psi^{\otimes N}\|\boldsymbol{G}^N) + D(|E_0^A\rangle\langle E_0^A|\|\gamma_A) - D(\boldsymbol{F}^N\|\boldsymbol{G}^N \otimes \gamma_A \otimes \tilde{\boldsymbol{G}}^N)\Big) \\ \geq& \frac{1}{\beta}\Big(D(\hat{\boldsymbol{P}}^N\|\hat{\boldsymbol{G}}^N) + H(\boldsymbol{P}^N) + D(|E_0^A\rangle\langle E_0^A|\|\gamma_A) - D(\hat{\boldsymbol{F}}^N\|\hat{\boldsymbol{G}}^N \otimes \hat{\gamma}_A \otimes \hat{\tilde{\boldsymbol{G}}}^N)\Big), \end{aligned} \tag{3.166}$$

where we have used the fact that

$$D(\psi^{\otimes N}\|\boldsymbol{G}^N) = D(\mathcal{D}(\psi^{\otimes N})\|\boldsymbol{G}^N) + D(\psi^{\otimes N}\|\mathcal{D}(\psi^{\otimes N})) = D(\hat{\boldsymbol{P}}^N\|\hat{\boldsymbol{G}}^N) + H(\boldsymbol{P}^N). \tag{3.167}$$

Next, we recall that $H(\boldsymbol{P}^N) = O(\log N)$ (see appendix 6.4 for details), and note that $D(|E_0^A\rangle\langle E_0^A|\|\gamma_A) = -\log\gamma_0^A$. Thus, the inequality from Eq. (3.166) can be simplified as follows:

$$\begin{aligned} F_{\text{diss}}^N \gtrsim& \frac{1}{\beta}\Big(D(\hat{\boldsymbol{P}}^N\|\hat{\boldsymbol{G}}^N) - D(\hat{\boldsymbol{F}}^N\|\hat{\boldsymbol{G}}^N \otimes \hat{\gamma}_A \otimes \hat{\tilde{\boldsymbol{G}}}^N) - \log\gamma_0^A\Big) \\ =& \frac{1}{\beta}\Big(H(\hat{\boldsymbol{F}}^N) - H(\hat{\boldsymbol{P}}^N) - \log(\tilde{D}D^A) - \log\gamma_0^A\Big). \end{aligned} \tag{3.168}$$

Here, $\tilde{D}$ and D^A denotes the embedding constants defined by Eq. (3.52) for $\tilde{\boldsymbol{G}}^N$ and γ_A, respectively. Similarly, we use D to represent the embedding constant for $\boldsymbol{G}^N$. We can choose $\tilde{D}$ and D to be equal because the only thing that matters is that $\tilde{G}_k^N = \tilde{D}_k/\tilde{D}$ and $G_k^N = D_k/D$. Therefore, a change in $\tilde{D}$ or D can be compensated by the appropriate change in $\tilde{D}_k$ or D_k. In addition, we note that $k = D\tilde{D}_k D_1^A = \tilde{D}\tilde{D}_k D_1^A$, which allows us to express the entropy of $\hat{\boldsymbol{F}}^N$.

$$\begin{aligned}
H(\hat{\boldsymbol{F}}^N) =& -\sum_{i=1}^{k} \frac{1-\epsilon}{k} \log\left(\frac{1-\epsilon}{k}\right) - \sum_{i>k} (\hat{\boldsymbol{P}}^N \otimes \boldsymbol{f}_0^A \otimes \tilde{\boldsymbol{\eta}})_i^{\downarrow} \log(\hat{\boldsymbol{P}}^N \otimes \boldsymbol{f}_0^A \otimes \tilde{\boldsymbol{\eta}})_i^{\downarrow} \\
=& -(1-\epsilon)\log(1-\epsilon) + (1-\epsilon)\log k - \sum_{i>k} (\hat{\boldsymbol{P}}^N \otimes \boldsymbol{f}_0^A \otimes \tilde{\boldsymbol{\eta}})_i^{\downarrow} \log\left(\frac{\hat{\boldsymbol{P}}^N}{\tilde{D}D_0^A}\right)_i^{\downarrow} \\
\simeq& \log k - \epsilon \log L - \sum_{i>L} (\hat{\boldsymbol{P}}^N)_i^{\downarrow} \log(\hat{\boldsymbol{P}}^N)_i^{\downarrow},
\end{aligned} \tag{3.169}$$

where in the last step we used the relation that $L = k/(\tilde{D}D_0^A)$, which comes from Eq. (3.135). Thus, from Eq. (3.168), the amount of dissipated free energy in the optimal distillation process is simply bounded by

$$\begin{aligned}
F_{\text{diss}}^N \gtrsim& \frac{1}{\beta}\left(\sum_{i=1}^{L} (\hat{\boldsymbol{P}}^N)_i^{\downarrow} \log(\hat{\boldsymbol{P}}^N)_i^{\downarrow} + \log\left(\frac{k}{\tilde{D}D^A}\right) - \epsilon \log L - \log \gamma_0^A\right) \\
=& \frac{1}{\beta}\left(\sum_{i=1}^{L} (\hat{\boldsymbol{P}}^N)_i^{\downarrow} \log(\hat{\boldsymbol{P}}^N)_i^{\downarrow} + (1-\epsilon)\log L\right).
\end{aligned} \tag{3.170}$$

Finally, employing the expression for L given in Eq. (3.154), we can express the above bound as

$$F_{\text{diss}}^N \gtrsim \frac{1}{\beta}\left(\sum_{i=1}^{L} (\hat{\boldsymbol{P}}^N)_i^{\downarrow} \log(\hat{\boldsymbol{P}}^N)_i^{\downarrow} + (1-\epsilon)\left(AN + x\sqrt{N v_N}\right)\right), \tag{3.171}$$

where A and x are given by Eq. (3.155).

3.5.5.2 Calculating bound for optimal dissipation

Now, we proceed to bound the first term on the right hand side of Eq. (3.171). We begin by noting that Eq. (3.160) implies that the following holds for any $\delta > 0$:

$$\sum_{i=1}^{L(x)} (\hat{\boldsymbol{P}}^N)_i^{\downarrow} \log(\hat{\boldsymbol{P}}^N)_i^{\downarrow} \geq \sum_{i=1}^{\chi_{\hat{\boldsymbol{P}}^N}(L(x+\delta))} (\hat{\boldsymbol{P}}^N)_i^{\downarrow} \log(\hat{\boldsymbol{P}}^N)_i^{\downarrow}. \tag{3.172}$$

Next, from the definition of $\chi_{\hat{\boldsymbol{P}}^N}(L(x+\delta))$, it follows that

$$\begin{aligned}
&\sum_{i=1}^{\chi_{\hat{\boldsymbol{P}}^N}(L(x+\delta))} (\hat{\boldsymbol{P}}^N)_i^{\downarrow} \log(\hat{\boldsymbol{P}}^N)_i^{\downarrow} = \sum_i \left\{ \hat{P}_i^N \log(\hat{P}_i^N) \,\middle|\, \hat{P}_i^N \geq \frac{1}{L(x+\delta)} \right\} \\
&= \sum_{\boldsymbol{k},g_{\boldsymbol{k}}} \left\{ \hat{P}^N_{\boldsymbol{k},g_{\boldsymbol{k}}} \log(\hat{P}^N_{\boldsymbol{k},g_{\boldsymbol{k}}}) \,\middle|\, \hat{P}^N_{\boldsymbol{k},g_{\boldsymbol{k}}} \geq \frac{1}{L(x+\delta)} \right\} = \sum_{\boldsymbol{k}} \left\{ P^N_{\boldsymbol{k}} \log(\hat{P}^N_{\boldsymbol{k},1}) \,\middle|\, P^N_{\boldsymbol{k}} \geq \frac{\prod_{i=1}^d D_i^{k_i}}{L(x+\delta)} \right\} \\
&= \sum_{\boldsymbol{k}} \left\{ P^N_{\boldsymbol{k}} \log(P^N_{\boldsymbol{k}}) \,\middle|\, P^N_{\boldsymbol{k}} \geq \frac{\prod_{i=1}^d D_i^{k_i}}{L(x+\delta)} \right\} - \sum_{\boldsymbol{k}} \left\{ P^N_{\boldsymbol{k}} \left(\sum_{j=1}^d k_j \log \gamma_j \right) \,\middle|\, P^N_{\boldsymbol{k}} \geq \frac{\prod_{i=1}^d D_i^{k_i}}{L(x+\delta)} \right\} \\
&\quad - (1-\epsilon) N \log D. \qquad (3.173)
\end{aligned}$$

Using the parametrization of $\boldsymbol{k}$ as a function of $\boldsymbol{s}$ given in Eq. (3.139), we can modify the constraint on the summand in Eq. (3.173) as follows:

$$\begin{aligned}
\log(P^N_{\boldsymbol{k}}) &\geq \sum_{i=1}^d k_i \log D_i - \log(L(x+\delta)) = \sum_{i=1}^d (Np_i + \sqrt{N} s_i) \log \gamma_i + N \log D - \log L(x+\delta) \\
&= -\beta\sqrt{N} \sum_{i=1}^d s_i E_i + N\Big(\log D - D(\psi\|\gamma)\Big) - N\Big(\log D - D(\psi\|\gamma)\Big) - (x+\delta)\sqrt{N v_N} \\
&= -\beta\sqrt{N} \sum_{i=1}^d s_i E_i - (x+\delta)\sqrt{N v_N} = -\beta\left(\sqrt{N}\boldsymbol{s}\cdot\boldsymbol{E} + \delta\sigma(F^N) + \Delta F^N\right), \qquad (3.174)
\end{aligned}$$

where the second equality in the equation above is obtained using the form of L given in Eq. (3.154) and Eq. (3.140). In the final equality, we use the definition $\sigma(F^N) = \sqrt{N v_n}/\beta$ and Eq. (3.155), which states that $x = \Delta F^N / \sigma(F^N)$. Furthermore, since $\log(P^N_{\boldsymbol{k}(\boldsymbol{s})}) = O(\log N)$, we can rewrite the condition from Eq. (3.174) as

$$\sqrt{N}\boldsymbol{s}\cdot\boldsymbol{E} + \Delta F^N + \delta\sigma(F^N) \gtrsim 0. \qquad (3.175)$$

Coming back, we can now rewrite Eq. (3.173) employing the parametrization of $\boldsymbol{k}$ as a function of $\boldsymbol{s}$ from Eq. (3.139) and re-expressing the constraint using Eq. (3.175):

$$\begin{aligned}
&\sum_{i=1}^{\chi_{\hat{\boldsymbol{P}}^N}(L(x+\delta))} (\hat{\boldsymbol{P}}^N)_i^{\downarrow} \log(\hat{\boldsymbol{P}}^N)_i^{\downarrow} \\
&= \sum_{\boldsymbol{k}(\boldsymbol{s})} \left\{ P^N_{\boldsymbol{k}(\boldsymbol{s})} \left(\log(P^N_{\boldsymbol{k}(\boldsymbol{s})}) - \sqrt{N} \sum_{i=1}^{d} s_i \log \gamma_i \right) \middle| \sqrt{N}\boldsymbol{s}\cdot\boldsymbol{E} + \Delta F^N + \delta\sigma(F^N) \geq 0 \right\} \\
&-(1-\epsilon)N\Big(\log D - D(\psi\|\gamma)\Big) \simeq \beta\sqrt{N} \sum_{\boldsymbol{s}} \left\{ P^N_{\boldsymbol{k}(\boldsymbol{s})} \boldsymbol{s}\cdot\boldsymbol{E} \middle| \sqrt{N}\boldsymbol{s}\cdot\boldsymbol{E} + \Delta F^N + \delta\sigma(F^N) \geq 0 \right\} \\
&-(1-\epsilon)AN, \qquad (3.176)
\end{aligned}$$

where we used the definition of A from Eq. (3.155).

Our next goal is then to evaluate the sum

$$\sum_{\boldsymbol{s}} \left\{ P^N_{\boldsymbol{k}(\boldsymbol{s})} \boldsymbol{s}\cdot\boldsymbol{E} \middle| \sqrt{N}\boldsymbol{s}\cdot\boldsymbol{E} + \Delta F^N + \delta\sigma(F^N) \geq 0 \right\}. \qquad (3.177)$$

We shall progress in a similar manner as before. In order to proceed, we will use a multivariate normal distribution $\mathcal{N}^{(\boldsymbol{\mu},\boldsymbol{\Sigma})}$ to approximate the multinomial distribution $\boldsymbol{P}^N$. The mean vector of this normal distribution is given by $\boldsymbol{\mu} = N\boldsymbol{p}$ and the covariance matrix is given by $\boldsymbol{\Sigma} = N(\text{diag}\,(\boldsymbol{p}) - \boldsymbol{p}\boldsymbol{p}^T)$.

$$\begin{aligned}
\mathcal{N}^{(\boldsymbol{\mu},\boldsymbol{\Sigma})}_{\boldsymbol{k}(\boldsymbol{s})} &= \frac{1}{\sqrt{(2\pi)^d|\boldsymbol{\Sigma}|}} \exp\left(-\frac{1}{2}(\boldsymbol{k}-\boldsymbol{\mu})^T\boldsymbol{\Sigma}^{-1}(\boldsymbol{k}-\boldsymbol{\mu})\right) \\
&= \frac{1}{\sqrt{(2\pi)^d|\boldsymbol{\Sigma}|}} \exp\left(-\frac{1}{2}\boldsymbol{s}^T N\boldsymbol{\Sigma}^{-1}\boldsymbol{s}\right). \qquad (3.178)
\end{aligned}$$

After obtaining the multivariate normal distribution $\mathcal{N}^{(\boldsymbol{\mu},\boldsymbol{\Sigma})}$ as an approximation to the multinomial distribution $\boldsymbol{P}^N$, the next step is to standardize it by applying rotation and scaling transformations as follows:

$$\boldsymbol{\Sigma} = \Theta^T\sqrt{\boldsymbol{\Lambda}}\sqrt{\boldsymbol{\Lambda}}\Theta, \qquad (3.179)$$

where $\boldsymbol{\Lambda}$ is a diagonal matrix with the eigenvalues of $\boldsymbol{\Sigma}$ and Θ is an orthogonal matrix with columns given by the eigenvectors of $\boldsymbol{\Sigma}$. This rotation and scaling of the axes enable us to write $\mathcal{N}^{(\boldsymbol{\mu},\boldsymbol{\Sigma})}$ as a product of univariate standard normal distribution $\phi(y_i)$:

$$\mathcal{N}^{(\boldsymbol{\mu},\boldsymbol{\Sigma})}_{\boldsymbol{k}(\boldsymbol{s}(\boldsymbol{y}))} = \frac{1}{\sqrt{(2\pi)^d|\boldsymbol{\Sigma}|}} \exp\left(-\frac{1}{2}\boldsymbol{y}^T\boldsymbol{y}\right) = \prod_{i=1}^{d}\phi(y_i), \qquad (3.180)$$

where

$$\boldsymbol{y} = \sqrt{N}(\Theta^T\sqrt{\Lambda})^{-1}\boldsymbol{s}, \qquad (3.181)$$

such that

$$\boldsymbol{s} = \frac{1}{\sqrt{N}}\Theta^T\sqrt{\Lambda}\boldsymbol{y}. \tag{3.182}$$

From Eq. (3.181) and Eq. (3.182), one can evaluate the sum given in Eq. (3.177) as follows:

$$\sum_{\boldsymbol{y}}\left\{P^N_{\boldsymbol{k}(\boldsymbol{s}(\boldsymbol{y}))}\frac{\tilde{\boldsymbol{E}}\cdot\boldsymbol{y}}{\sqrt{N}}\middle|\tilde{\boldsymbol{E}}\cdot\boldsymbol{y}+\Delta F^N+\delta\sigma(F^N)\geq 0\right\}, \tag{3.183}$$

where we defined $\tilde{\boldsymbol{E}} := \sqrt{\Lambda}\Theta\boldsymbol{E}$ with the normalisation

$$\|\tilde{\boldsymbol{E}}\| = \sqrt{\tilde{\boldsymbol{E}}\cdot\tilde{\boldsymbol{E}}} = \sqrt{(\sqrt{\Lambda}\Theta\boldsymbol{E})\cdot(\sqrt{\Lambda}\Theta\boldsymbol{E})} = \sqrt{\boldsymbol{E}\cdot\Theta^T\Lambda\Theta\boldsymbol{E}} = \sqrt{\boldsymbol{E}\cdot\boldsymbol{\Sigma}\boldsymbol{E}} = \sigma(F^N). \tag{3.184}$$

We can then equivalently write Eq. (3.183) as

$$\frac{\sigma(F^N)}{\sqrt{N}}\sum_{\boldsymbol{y}}\left\{P^N_{\boldsymbol{k}(\boldsymbol{s}(\boldsymbol{y}))}\hat{\tilde{\boldsymbol{E}}}\cdot\boldsymbol{y}\;\middle|\;\sigma(F^N)\hat{\tilde{\boldsymbol{E}}}\cdot\boldsymbol{y}+\Delta F^N+\delta\sigma(F^N)\geq 0\right\}, \tag{3.185}$$

where $\hat{\tilde{\boldsymbol{E}}}$ is unit vector in the direction $\tilde{\boldsymbol{E}}$. Now, we choose a rotation R such that

$$R\hat{\tilde{\boldsymbol{E}}} = (1,\dots,0)^T \tag{3.186}$$

and we call $R\boldsymbol{y} = \boldsymbol{x}$. Hence, we can re-express Eq. (3.185) as

$$\begin{aligned}&\frac{\sigma(F^N)}{\sqrt{N}}\sum_{\boldsymbol{y}}\left\{P^N_{\boldsymbol{k}(\boldsymbol{s}(\boldsymbol{y}))}R\hat{\tilde{\boldsymbol{E}}}\cdot R\boldsymbol{y}\;\middle|\;\sigma(F^N)R\hat{\tilde{\boldsymbol{E}}}\cdot R\boldsymbol{y}+\Delta F^N+\delta\sigma(F^N)\geq 0\right\}\\ &=\frac{\sigma(F^N)}{\sqrt{N}}\sum_{\boldsymbol{x}}\left\{P^N_{\boldsymbol{k}(\boldsymbol{s}(\boldsymbol{x}))}x_1\;\middle|\;\sigma(F^N)x_1+\Delta F^N+\delta\sigma(F^N)\geq 0\right\}.\end{aligned} \tag{3.187}$$

By using the multivariate normal distribution approximation and its isotropy, we can precisely compute the expression above through an integral over $\boldsymbol{x}$ with the following form:

$$\frac{\sigma(F^N)}{\sqrt{N}}\left(\int_{-\infty}^{+\infty}dx_2\phi(x_2)\dots\int_{-\infty}^{+\infty}dx_d\phi(x_d)\int_{-\infty}^{d_{\mathcal{O}}}dx_1x_1\phi(x_1)\right) = \frac{\sigma(F^N)}{\sqrt{2\pi N}}\exp\left(-\frac{d_{\mathcal{O}}^2}{2}\right), \tag{3.188}$$

where $d_{\mathcal{O}}$ is the distance between the hyperplane specified by the constraint given in Eq. (3.187) and the origin:

$$d_{\mathcal{O}} = \frac{\Delta F^N+\delta\sigma(F^N)}{\sqrt{\tilde{\boldsymbol{E}}\cdot\tilde{\boldsymbol{E}}}} = \frac{\Delta F^N}{\sigma(F^N)}+\delta. \tag{3.189}$$

Thus, finally we obtain the following expression for the desired sum from Eq. (3.177):

$$\sum_{\boldsymbol{s}} \left\{ P^N_{\boldsymbol{k}(\boldsymbol{s})} \boldsymbol{s}\cdot\boldsymbol{E} \middle| \sqrt{N}\boldsymbol{s}\cdot\boldsymbol{E} + \Delta F^N + \delta\sigma(F^N) \geq 0 \right\} = \frac{\sigma(F^N)}{\sqrt{2\pi N}} \exp\left(-\frac{1}{2}\left(\frac{\Delta F^N}{\sigma(F^N)} + \delta\right)^2\right). \tag{3.190}$$

Substituting the above to Eq. (3.176), and the resulting expression to Eq. (3.172), we obtain the following bound:

$$\sum_{i=1}^{L(x)} (\hat{\boldsymbol{P}}^N)^{\downarrow}_i \log(\hat{\boldsymbol{P}}^N)^{\downarrow}_i \gtrsim -(1-\epsilon)A + \frac{\beta\sigma(F^N)}{\sqrt{2\pi}} \exp\left(-\frac{1}{2}\left(\frac{\Delta F^N}{\sigma(F^N)} + \delta\right)^2\right), \tag{3.191}$$

which can be used in Eq. (3.171) to write the following:

$$F^N_{\text{diss}} \gtrsim \frac{\sigma(F^N)}{\sqrt{2\pi}} \exp\left(-\frac{1}{2}\left(\frac{\Delta F^N}{\sigma(F^N)} + \delta\right)^2\right) + (1-\epsilon)\Delta F^N. \tag{3.192}$$

Since the above holds for any $\delta > 0$, by taking the limit $\delta \to 0$, we finally obtain

$$F^N_{\text{diss}} \gtrsim (1-\epsilon)\Delta F^N + \frac{\sigma(F^N)}{\sqrt{2\pi}} \exp\left(-\frac{(\Delta F^N)^2}{2\sigma(F^N)^2}\right). \tag{3.193}$$

Using Eq. (3.163) we have

$$\Delta F^N = -\Phi^{-1}(\epsilon)\sigma(F^N), \tag{3.194}$$

and so substituting this in Eq. (3.193) we finally arrive at

$$F^N_{\text{diss}} \gtrsim a(\epsilon)\sigma(F^N), \tag{3.195}$$

with a given by Eq. (3.29), which completes the proof.

3.6 Outlook

This chapter presents a new version of the fluctuation-dissipation theorem for state interconversion via thermal operations. The optimal transformation error and the amount of free energy dissipated during the process are related to fluctuations in the initial state's free energy. The problem is tackled in two regimes: pure and energy-incoherent initial states, both of which are transformed into an energy eigenstate. The possibility of altering the Hamiltonian during the process is also considered. In the case of several independent, non-identical energy-incoherent systems, a single-shot upper bound on the optimal transformation error is presented as a function of free energy fluctuations and average dissipated free energy.

In the asymptotic regime, the optimal transformation error is obtained up to second-order asymptotic corrections [63]. This extends previous research to non-identical initial systems and varying Hamiltonians. Additionally, the asymptotic analysis of the thermodynamic distillation process from quantum states with coherence in the energy eigenbasis is performed for the first time. The optimal transformation error from identical pure states and the free energy dissipated during the transformation are expressed as a function of free energy fluctuations up to second-order asymptotic corrections.

Our work can be naturally extended in the following directions. Firstly, one could generalise our analysis to arbitrary initial states. We indeed believe that an analogous result to ours will hold for such general mixed states with coherence. That is because dephasing into fixed energy subspaces leads to free energy change of the order $O(\log N)$, which is negligible compared to the second order asymptotic corrections of the order $O(\sqrt{N})$ that we focus on. In other words, the contribution of coherence to free energy per copy of the system vanishes faster with growing N than what we are interested while studying second order corrections.

Secondly, it would be extremely interesting to generalise the thermodynamic state interconversion problem to arbitrary final states, and see how the interplay between the fluctuations of the initial and target states affects dissipation. For energy-incoherent initial and final states one can infer from [108] that appropriately tuned fluctuations can significantly reduce dissipation, however nothing is known for states with coherence. Unfortunately, since thermal operations are time-translation covariant, such that coherence and athermality form independent resources [89, 124, 125], it seems unlikely that the current approach can be easily generalised. Thirdly, one could try to extend our results on pure states to allow for non-identical systems and to derive a bound working for all N, not only for $N \to \infty$ (i.e., replace the proving technique based on central limit theorem by the one based on a version of Berry-Esseen theorem).

In our work we have also provided a number of physical applications of our fluctuation-dissipation theorems by considering several scenarios and explaining how our results can be useful to describe fundamental and well-known thermodynamic and information-theoretic processes. We derived the optimal value of extractable work in a thermodynamic distillation process as a function of the transformation error associated to the work quality. This, together with the knowledge of the actual final free energy of the battery system provided by theorem 26B, could potentially be used to clarify the notion of imperfect work [87, 126, 127], and to construct a comparison platform allowing one to continuously distinguish between work-like and heat-like forms of energy. We have also shown how our results yield the optimal trade-off between the work invested in erasing N independent bits prepared in arbitrary states, and the erasure quality measured by the infidelity distance between the final state and the fully erased state. This can of course be straightforwardly extended to higher-dimensional systems and arbitrary final erased state (not necessarily the ground state). Finally, we have investigated the optimal encoding rate into a collection of non-interacting subsystems consisting of energy-incoherent or pure states using thermal operations. We derived the optimal rate (up to second-order asymptotics) of encoding information with a given average decoding error and without spending thermodynamic resources. This provides an operational interpretation of the resourcefulness of athermal quantum states for communication scenarios under the restriction of using thermal operations.

We would also like to point out to some possible technical extensions of our results. Firstly, we used infidelity as our quantifier of transformation error, but we expect that similar results could be derived using other quantifiers, e.g., the trace distance. Secondly, our investigations were performed in the spirit of small-deviation analysis (where we look for constant transformation error and total free energy dissipation of the order $O(\sqrt{N})$), but possibly other interesting fluctuation-dissipation relations could be derived within the the moderate and large deviation regimes. Thirdly, our result for pure states is limited to Hamiltonians with incommensurable spectrum, but we believe this is just a technical nuisance that one should be able to get rid of. Lastly, within the framework of general resource theories, it might be possible to derive analogous fluctuation-dissipation relations, but with free energy replaced by a resource quantifier relevant for a given resource theory.

Chapter 4

Extraction of ergotropy

4.1 Introduction

The second law of thermodynamics sets a limit on the amount of work that can be done by macroscopic systems by using the change in free energy. On the other hand, in microscopic scenarios, the concept of ergotropy plays a similar role. Ergotropy refers to the maximum amount of energy that can be obtained from a system through a unitary operation. This energy can then be stored as work in a suitable work storage, or *battery*. If a state has zero ergotropy, it means that no energy can be extracted and stored as work, and it is referred to as a *passive state* [128]. This concept is crucial in quantum thermodynamics since it sets a fundamental limit on the average amount of work that can be extracted from a system.

The concept of ergotropy plays a vital role in various fields of quantum thermodynamics. Firstly, it characterizes the optimal energy that can be extracted from quantum batteries, as evidenced in several studies such as [129, 130, 131, 132, 133]. Recent research has also linked ergotropy to coherence measures [134] and relative entropy [135]. However, it is essential to note that ergotropy is not always additive, leading to the notion of *complete passivity*. A state is said to be completely passive if the ergotropy of the state, consisting of an arbitrary number of its copies, is also passive. This concept connects the idea of ergotropy to the equilibrium state since any completely passive state must have a Gibbs form [136]. Additionally, recent studies have shown that complete passivity is linked to the inability to extract energy, even in the presence of a catalyst [137].

This chapter aims to investigate how much ergotropy a system can acquire through its interaction with a heat bath in a thermodynamically free manner. In simpler terms, we want to induce ergotropy to a system that is in contact with the heat bath through thermal operation. We have discussed thermal operation in detail in chapter 2 [70, 71, 138]. The objective is to utilize the heat bath as a source of heat that can be converted into work by a microscopic heat engine, which we will explore in the next chapter (refer to chapter 5). Additionally, since ergotropy measures the degree of population inversion within a system, non-Markovian evolution is necessary for its extraction. This also justifies the process of inducing ergotropy to a system using the thermal operation framework.

We have two objectives: first, to establish a connection between the extraction of ergotropy and the Second Law of Thermodynamics, and second, to quantitatively characterize the process of ergotropy extraction for systems of both finite and infinite dimensions. We will determine the fundamental limit on the amount of ergotropy that can be extracted from the bath via thermal operation and express it as the difference of non-equilibrium free energy. We will also present an example in which this limit is reached when the dimension of the system's Hamiltonian approaches infinity.

4.2 Defining work as a change of average energy

The consumption or extraction of work is a central focus of thermodynamics, referring to the input or output of ordered energy to a system. In chapter 2, section 2.4, we extensively discussed the concept of work in both equilibrium and non-equilibrium scenarios. In the context of the resource theory of athermality, we introduced the ideas of single-shot and deterministic work extraction. As we described, the work done by a system can be envisioned as a result of enhancing its potential energy, such as the potential energy of a hanging weight that experiences a height difference. It is well-known that work cannot be extracted solely from a thermal reservoir, but if two reservoirs at different temperatures are available, it is possible to design protocols to extract work. One common example is a heat engine, where a machine interacts with two heat baths sequentially, undergoing a cyclic process.

The concept of single shot and deterministic work extraction has been discussed in the context of the resource theory of athermality (refer to section 2.4.3) where the description involves representing the work storage as a two-level system. In that scenario work does not fluctuate. The method of using thermomajorization as an application to obtain work bounds has limitations since it only works when the energy gap of the two-level work storage is predetermined. Therefore, this method is unsuitable for non-deterministic work extraction, which is the main topic of focus in this chapter.

The process of extracting work from a system where the energy change is subject to random processes, such as thermalization, is known as non-deterministic work extraction. To model this process, we represent the weight as a quantum system described by a density matrix ρ_W that undergoes a change to $\tilde{\rho}_W$ during the thermodynamic process.

The amount of work extracted is then defined as the difference between the average energy of the battery before and after the process, which is given by the following relation:

$$W := \mathrm{Tr}(H_W \tilde{\rho}_W) - \mathrm{Tr}(H_W \rho_W), \tag{4.1}$$

where H_W is the Hamiltonian of the battery.

Since the amount of work extracted depends on fluctuating processes, it is treated as a random variable. It has been shown that, despite the randomness, an optimal amount of average work can be extracted, which is equal to the free energy of the system [79]. Additionally in [79], it has been shown that the Carnot efficiency can be achieved, which is the maximum possible efficiency for a heat engine operating between two temperature reservoirs.

The definition of work provided in Eq. (4.1) is simple, making it easier to analyze. However, it is important to separately consider the amount of entropy when using this measure to ensure that contributions from heat to the average energy increase are negligible or accounted for. This is necessary because thermodynamic processes can produce work with fluctuations of the same order. These fluctuations are undesirable for two reasons:

1. Firstly, they can impact the battery's reusability, as the full amount of W may not be extractable as these fluctuation results dissipation of certain amount of energy.

2. Secondly, the battery may have been used as an entropy sink, which cannot be captured by the average work. This could result in an apparent violation of the second law of thermodynamics.

The second problem mentioned above has been addressed recently by a new approach [79, 139], which constrains the set of allowed operations to satisfy *translational invariance* with respect to the battery. This refinement helps to formulate a more precise version of the second law. We will provide a brief description of the translational invariant model of the battery in the next section.

Although this approach is a notable progress in justifying the usage of average energy as a measure of work, there are still various aspects that need improvement. For instance, the battery models used in this approach presently do not have a ground state, which is only a sensible assumption when the initial and final states of the battery possess exceedingly high energy. Therefore, it is crucial to comprehend the corrections that emerge when we employ physical battery models.

4.3 Translationally invariant model of work storage

In this section, we describe the translationally invariant model of the work storage or battery. This model is sometimes referred to as *weight* since this models resembles lifting a mass slowly such that work done is given by the change of potential energy. We start with the definition.

Definition 29 (Ideal weight)**.** A ideal weight in the state ρ_W is modelled by a Hamiltonian

$$H_W = \epsilon \sum_{j\in\mathbb{Z}} j|j\rangle\langle j| \tag{4.2}$$

where $\epsilon > 0$ and $\mathbb{Z}$ is the set of integers. We denote the generator of translation in the energy referred as *shift* operator

$$\Gamma_a := \sum_{j\in\mathbb{Z}} |j+a\rangle\langle j|. \tag{4.3}$$

First, let us characterize the type of operation that we consider and show that they are suitably general and implementable to encompass what is commonly considered to be thermodynamics.

Lemma 33 (Lemma 2 of [139])**.** *Let $\mathcal{H}_S$ be finite-dimensional Hilbert space with dimension d and*

$$H_S = \epsilon\Sigma_{n=1}^{d} z_n|\psi_n\rangle\langle\psi_n| \tag{4.4}$$

is the Hamiltonian of the system in the Hilbert space $\mathcal{H}_S$. Let $\mathcal{H}_W$ is an infinite-dimensional Hilbert space associated with ideal weight H_W as introduced in definition 29. Let $\mathcal{LT}(H_S+H_W)$ be the set of all bounded linear operator X acting on $\mathcal{H}_S\otimes\mathcal{H}_W$ that X satisfies

1. *Energy conservation: $[X, H_S+H_W]=0$.*

2. *Translational invariance: $\forall a\in\mathbb{Z}$ it satisfies $[X, \mathbb{I}_S\otimes\Gamma_a]=0$.*

Define the mapping $G:\mathcal{L}(\mathcal{H}_s)\to\mathcal{LT}(H_S+H_W)$

$$G(V) := \sum_{n,n'}^{d} \langle\psi_n|V|\psi_{n'}\rangle|\psi_n\rangle\langle\psi_{n'}|\otimes\Gamma_{(z_{n'}-z_n)}, \tag{4.5}$$

where $\mathcal{L}(\mathcal{H}_S)$ as the set of linear operator acting on $\mathcal{H}_S$. The mapping G is a bijective, with the following properties.

$$\begin{aligned} G(\alpha A+\beta B) &= \alpha G(A)+\beta G(B) \\ G(AB) &= G(A)G(B) \\ G(A^\dagger) &= (G(A))^\dagger \\ G(\mathbb{I}_S) &= \mathbb{I}_S\otimes\mathbb{I}_W \end{aligned} \tag{4.6}$$

Proof. Let $G(V)$ be a finite sum of bounded linear operators, and assume $[\Gamma_a, \Gamma_{a'}]=0$ for all $a, a'\in\mathbb{Z}$. It then follows that $[G(V), \mathbb{I}_S\otimes\Gamma_a]=0$ for all $a\in\mathbb{Z}$, as well as $[G(V), H_S+H_W]=0$

from the relation $[H_W, \Gamma_a] = \epsilon a \Gamma_a$. Therefore, we have $G(\mathcal{L}(\mathcal{H}_S)) \subseteq \mathcal{LT}(H_S + H_W)$, and it is straightforward to verify the properties given in Eq. (4.6). To prove that the map G is bijective, we must show injectivity and surjectivity. To prove injectivity, suppose $G(V_1) = G(V_2)$. The orthonormality of $|\psi_n\rangle$ and the fact that $\Gamma_a \neq 0$ for all a implies that $V_1 = V_2$, proving injectivity. To prove surjectivity, take any $Y \in \mathcal{LT}(H_S + H_W)$ with $[Y, H_S + H_W] = 0$. From the eigen decomposition of $H_S + H_W$, we have $H_S + H_W = \epsilon \sum_{j \in \mathbb{Z}} j P_j$, where $P_j = \sum_{n=1}^{d} |\psi_n\rangle\langle\psi_n| \otimes |j - z_n\rangle\langle j - z_n|$. It then follows that $Y = \sum_{j \in \mathbb{Z}} P_j Y P_j$. Hence, we have

$$Y = \sum_j \sum_{n,n'} \langle\psi_n|\langle j - z_n|Y|\psi_n'\rangle|j - z_{n'}\rangle|\psi_n\rangle\langle\psi_{n'}| \otimes |j - z_n\rangle\langle j - z_{n'}| \tag{4.7}$$

Using $|j - z_n'\rangle = \Gamma_j| - z_{n'}\rangle$ and $(\mathbb{1}_S \otimes \Gamma_j^\dagger)Y(\mathbb{1}_S \otimes \Gamma_j) = Y$, we obtain

$$X = \sum n, n' \langle\psi_n|\langle -z_n|Y|\psi_n'\rangle| - z_{n'}\rangle|\psi_n\rangle\langle\psi_{n'}|, \tag{4.8}$$

such that $G(X) = Y$, proving the lemma. □

Using this lemma, we can demonstrate that the set of unitary operations acting on the Hilbert space $\mathcal{H}_S$ is equivalent to the unitaries that commute with the Hamiltonian $H_S + H_W$. Therefore, any reduction in the average energy of a system by a unitary operation can be stored as work in a battery that satisfies translational invariance. This result is essential for analyzing work extraction and optimizing the performance of quantum heat engines. In the next section, we will introduce the concept of ergotropy and establish the second law as an upper limit on the change of ergotropy with respect to free energy.

4.4 Ergotropy and second law

The second law of thermodynamics provides a framework for understanding the transformations that a thermodynamic system can undergo as it exchanges heat and work with its environment. These transformations are governed by thermodynamic potentials, which set fundamental limits on energy conversions in thermodynamic processes, regardless of the microscopic details. These limits establish upper bounds on power and efficiency. One such crucial thermodynamic potential is free energy, which we have already encountered in earlier chapters as it is crucial for describing work bounds. However, for the sake of convenience, we will define it again here.

Definition 30 (Free energy)**.** We defined the free energy of a system in a state ρ, which is in contact with a thermal bath.

$$F(\rho) = E(\rho) - \frac{1}{\beta} S(\rho), \tag{4.9}$$

where $E(\rho)$ is the average energy, $S(\rho)$ is von Neumann entropy, and β is the inverse temperature of the bath.

Chapters 1 and 2 offer several physical scenarios that exemplify the reliable forecasting of equilibrium state transitions by free energy when a system is in contact with a thermal bath. In the absence of any external driving force, the system always reduces its free energy, ultimately achieving equilibrium at the minimum. Moreover, if the system can perform work, the maximum amount of work that can be extracted is determined by the free energy, as established by the well-known inequality (4.10) in classical thermodynamics (refer to Eq. (2.76)). The inequality is given by:

$$W \geq \Delta F. \tag{4.10}$$

Let us refer to the average work $\langle W \rangle$ as W for simplicity. This inequality is powerful as it establishes a lower bound on the amount of work needed to accomplish a desired change in free energy. Inequality in Eq. (4.10) has been derived for both weakly [87] and strongly coupled [140, 141] systems, as well as in the context of thermal operations, where work storage is explicitly introduced [79, 142]. Interestingly, inequality (4.10) can also be expressed as the Jarzynski equality when free energy is treated as the fluctuating quantity [27, 109, 143, 104].

When a thermal system is disconnected from its reservoir or if the reservoir's size is finite, it is impossible to attain the maximum value permitted by the inequality (4.10). Consequently, this places a constraint on the quantity of work that can be generated, which is less than the change in free energy. In order to overcome this limitation, Allahverdyan et al. [128] proposed the concept of ergotropy as a new thermodynamic potential for an isolated system that undergoes a cyclic force with identical initial and final Hamiltonians. We define ergotropy as follows:

Definition 31 (Ergotropy)**.** The ergotropy of a system described by Hamiltonian H in the state ρ is defined as

$$R(\rho) = E(\rho) - \min_{U} E(U\rho U^{\dagger}) = E(\rho) - E(\rho_P), \tag{4.11}$$

where $E(\,\cdot\,) = \mathrm{Tr}(H\,\cdot\,)$ describes the average energy, and the minimum is taken over all unitary operators U acting on the Hilbert space of the system.

If $\rho = \sum_{i=1}^{d} p_i |i\rangle\langle i|$ and $H = \sum_{j=1}^{d} E_j |E_j\rangle\langle E_j|$ then it is straightforward to see that ρ_P is given by

$$\rho_P = \sum_{i=1}^{d} p_i^{\downarrow} |E_i^{\uparrow}\rangle\langle E_i^{\uparrow}| \tag{4.12}$$

where $p_1^{\downarrow} \geq p_2^{\downarrow} \geq \ldots \geq p_d^{\downarrow}$ and $E_1^{\uparrow} \leq E_2^{\uparrow} \leq \ldots \leq E_d^{\uparrow}$. From now on we shall take the

Hamiltonian with spectrum that satisfies $E_d \geq E_{d-1} \geq \dots E_2 \geq E_1$.

We refer to the state ρ_P as the *passive* state corresponding to the state ρ, and the quantity $E(\rho_P)$ is known as the *passive* energy of the state ρ. If the state ρ is diagonal, the minimization process can be restricted to the set of permutations [144]. The seminal work by Allahverdyan et al. [128] established a direct relationship between ergotropy and free energy.

The concept of ergotropy is closely related to the ideal weight model of energy storage that we introduced in section 4.3. This model was proposed in [79, 139] as a way of constructing a thermodynamic framework that satisfies the Second Law. Using lemma 4.3, we demonstrated that any unitary transformation applied to the system corresponds to an energy-conserving unitary (i.e., one that commutes with the system's Hamiltonian plus weight). Therefore, the work required to store a system's ergotropy can be stored in the translationally invariant weight.

In [79, 139] demonstrated that the work W required to lift the weight (and increase its average energy) is always less than the difference of free energy of the quantum state ρ and thermal state of the system γ in contact with a thermal reservoir.

$$-W \leq F(\rho) - F(\gamma_\beta) = \frac{1}{\beta} S(\rho \| \gamma_\beta), \tag{4.13}$$

Here γ_β is the Gibbs state at inverse temperature of the bath β and relative entropy $S(\rho\|\gamma_\beta)$ is given by

$$S(\rho\|\gamma_\beta) = \mathrm{Tr}\big(\rho(\log\rho - \log\gamma)\big). \tag{4.14}$$

This result was later extended to an arbitrary initial state of the weight and system's correlation, and the obtained work was formulated as [145]:

$$W = \Delta R = R(\sigma_f) - R(\sigma_i), \tag{4.15}$$

where ΔR represents a variation in the ergotropy of the so-called *effective control-marginal state* of the system, denoted by $\sigma_{i,f}$ (with subscripts i and f denoting initial and final states, respectively). The state $\sigma_{i,f}$ contains information regarding coherences and correlations that influence the process of work extraction [145]. This Eq. (4.15) highlights the correlation between ergotropy of the system and the translational symmetry of the ideal weight model. Furthermore, a formulation of the *tight second law* based on Eq. (4.15) is presented, which incorporates the ultimate bound stated in Eq. (4.13), but with adjustments that account for the influences of initial coherences and the size of the heat bath, as described in [146].

Since ergotropy can be understood as work done by the system, it is worth exploring its relevance in the operation of quantum thermal machines that we shall do in the next chapter. In the next section we shall explore the relation between free energy and ergotropy.

4.5 Ergotropy and free energy

We start by describing the established bounds on ergotropy of an isolated system [129] and system coupled with a bath [146] and their saturation.

The relationship between free energy and ergotropy, defined in Eq. (4.9) and Eq. (4.11), can be expressed as follows. Since entropy remains unchanged under unitary evolution, we can see that

$$\begin{aligned} R(\rho) &= E(\rho) - E(\rho_P) = E(\rho) - \frac{1}{\beta}S(\rho) + \frac{1}{\beta}S(\rho_P) - E(\rho_P) \\ &= F(\rho) - F(\rho_P) = \frac{1}{\beta}\big(S(\rho\|\gamma_\beta) - S(\rho_P\|\gamma_\beta)\big), \end{aligned} \tag{4.16}$$

where ρ_P refers to the passive state of the system defined in Eq. (4.11). Moreover, the relative entropy is defined in Eq. (4.14). It should be noted that the above equation holds true for any arbitrary value of β.

The Gibbs state that minimizes the average energy among states with fixed entropy. This can be utilized in Eq. (4.16) to minimize the free energy component. This leads to the following inequality:

$$R(\rho) = F(\rho) - F(\rho_P) \leq F(\rho) - F(\gamma_{\beta^*}) = \frac{1}{\beta}S(\rho|\gamma_{\beta^*}), \tag{4.17}$$

where the value of the inverse temperature β^* is uniquely determined by the relation $S(\rho) = S(\gamma_{\beta^*})$. It is important to note that the bound cannot be achieved in a single-shot scenario if the spectrum of ρ differs from that of γ_{β^*}. In such a case, it is impossible to obtain γ_{β^*} from ρ_P through a unitary transformation. However, Alicki and Fannes showed in [129] that this bound can be achieved by processing asymptotically many number of copies of the state ρ, i.e.,

$$\lim_{N\to\infty} \frac{1}{N}R(\rho^{\otimes N}) = F(\rho) - F(\gamma_{\beta^*}) = \frac{1}{\beta^*}S(\rho\|\gamma_{\beta^*}). \tag{4.18}$$

In [146] the bound on ergotropy has been established for a scenario where the system is coupled with a heat bath. To describe this briefly let us consider a system in the state ρ, which is connected to a thermal bath in the Gibbs state τ_β at inverse temperature of β. The composite state of the system and the bath can be expressed as a product, i.e., $\rho \otimes \tau_\beta$. Employing Eq. (4.16), we can establish the upper bound on the ergotropy of $\rho \otimes \tau_\beta$ in the following manner

$$\begin{aligned}
R(\rho \otimes \tau_\beta) &= F(\rho \otimes \tau_\beta) - F((\rho \otimes \tau_\beta)_P) \\
&= F(\rho \otimes \tau_\beta) - F(\gamma_\beta \otimes \tau_\beta) + F(\gamma_\beta \otimes \tau_\beta) - F((\rho \otimes \tau_\beta)_P) \\
&= \frac{1}{\beta} S(\rho \| \gamma_\beta) - \frac{1}{\beta} S((\rho \otimes \tau_\beta)_P \| \gamma_\beta \otimes \tau_\beta) \\
&\leq \frac{1}{\beta} S(\rho \| \gamma_\beta) = F(\rho) - F(\gamma_\beta),
\end{aligned} \tag{4.19}$$

where γ_β is the Gibbs state of the system with respect to the inverse temperature of the bath β. We can observe that the bound given in Eq. (4.19) is similar with the bound given in Eq. (4.17). The only difference is that the inverse temperature β is now fixed and given by the bath. In the literature, such a bound has been explored in [79, 146], where the saturation of the bound is achieved for a quasi-reversible process that consists of an infinite number of steps that conserves the total average energy of the system and bath, and assumes the existence of an infinitely large heat bath.

4.6 Free energy bound for ergotropy extraction

In the preceding section, we explored the bounds of ergotropy for systems that are either isolated or linked to an equilibrium bath. These bounds and their attainability establish a correspondence between a system's ergotropy and its non-equilibrium free energy, illustrated by Eq. (4.17) and Eq. (4.19). Consequently, ergotropy can be viewed as a universalization of free energy for finite-dimensional quantum systems, as described in [146].

Moving on to this section, we will address the question of how much ergotropy can be extracted through a system's coupling with a heat bath. In other words, what is the maximum amount of non-passivity that can be induced in a system via an interaction with the heat bath? We will begin by defining ergotropy extraction.

Definition 32 (Ergotropy extraction)**.** We define ergotropy extraction for a state ρ that transforms via a CPTP map Φ as the difference of ergotropy between initial and final state, i.e,

$$R(\Phi(\rho)) - R(\rho). \tag{4.20}$$

In this chapter, we will be interested in inducing non-passivity in a system through an interaction with a single heat bath, and we assume the total energy of the system and bath to be conserved. As a consequence, we consider CPTP maps Φ to be a thermal operation [33, 70, 71] as introduced in definition 2.6 i.e.,

$$\Phi(\rho) = \mathrm{Tr}_B(U(\rho \otimes \tau_\beta)U^\dagger), \tag{4.21}$$

such that $[U, H_S + H_B] = 0$, where H_S and H_B are the Hamiltonian of the system and the bath, respectively. As mentioned earlier, τ_β is the Gibbs state of the bath at inverse temperature β. Thermal operations constitute a subclass of a bigger set of transformations called Gibbs-preserving maps, which are defined as follows:

Definition 33 (Gibbs preserving map)**.** Consider a complete positive trace-preserving map Φ is acting on a d- dimensional quantum system with Hamiltonian H_S that is in contact with a heat bath at inverse temperature β. Φ is said to be a Gibbs preserving map if and only if

$$\Phi(\gamma_S) = \gamma_S, \tag{4.22}$$

where γ_S is the Gibbs state of the system i.e., $\gamma_S = \frac{e^{-\beta H_S}}{Z_S}$ with $Z_S = \mathrm{Tr}(e^{-\beta H_S})$.

The sets of Gibbs preserving maps and thermal operations are the same when their action is restricted to states ρ that are diagonal in the energy eigenbasis i.e., $[\rho, H_S] = 0$. On the other hand, if there is coherence in the state of the system i.e., $[\rho, H_S] \neq 0$ they are not same [147]. In this chapter and the next chapter, we shall deal with the states that are diagonal in energy eigenbasis i.e., $[\rho, H_S] = 0$.

Before discussing ergotropy extraction via Gibbs-preserving maps, we will propose a bound on the extraction of ergotropy for a general CPTP (completely positive, trace-preserving) map.

Proposition 34. *Let us assume an arbitrary state ρ that is evolving via a CPTP map Φ. Then, the ergotropy of the final state $\Phi(\rho)$ can be broken up into three contributions in the following term:*

$$R(\Phi(\rho)) = \frac{1}{\beta} S(\rho\|\gamma_\beta) - \frac{1}{\beta} S(\Phi(\rho)_P\|\gamma_\beta) - \frac{1}{\beta}\left(S(\rho\|\gamma_\beta) - S(\Phi(\rho)\|\gamma_\beta)\right), \tag{4.23}$$

where γ_β is a Gibbs state of the system at some inverse temperature β.

The formula (4.23) follows from the application of the identities given in Eq. (4.16) :

$$R(\Phi(\rho)) = F(\Phi(\rho)) - F(\Phi(\rho)_P), \quad ; \quad \frac{1}{\beta} S(\rho\|\gamma_\beta) = F(\rho) - F(\gamma_\beta). \tag{4.24}$$

The Eq. (4.23) can be divided into three distinct terms that contributes to the ergotropy of the final state $\Phi(\rho)$. The first term, $\frac{1}{\beta} S(\rho\|\gamma_\beta)$, represents the difference in free energy between the initial state ρ and the Gibbs state γ_β. This equation has already been used in the derivation of ergotropy bounds (refer to Eq. (4.17) and Eq. (4.19)) and presents the maximum bound for work extraction from a single heat bath (refer to Eq. (4.13)).

The second term, $-\frac{1}{\beta} S(\Phi(\rho)_P\|\gamma_\beta)$, is always non-positive due to the non-negativity of the relative entropy. This term represents the thermodynamic distance between the final passive state from equilibrium state. In particular, this term is zero if and only if the final state $\Phi(\rho)$ has the same spectrum as the Gibbs state, so that $\Phi(\rho)_P = \gamma_\beta$.

The final term can be interpreted as the entropy production for the CPTP map Φ:

$$\frac{1}{\beta}\left(S(\Phi(\rho)\|\gamma_\beta) - S(\rho\|\gamma_\beta)\right) = F(\Phi(\rho)) - F(\rho). \tag{4.25}$$

For thermal operations given by Eq. (4.21), the change in the energy of the system can be described as the amount of heat consumed from the bath i.e., $\Delta E = Q$, and then $F(\Phi(\rho)) - F(\rho) = Q - \frac{1}{\beta}\Delta S$ where ΔS denotes the change in the von Neumann entropy. Assuming the map Φ to be Gibbs-preserving leads to an important corollary.

Corollary 35. *Let us consider CPTP map Φ is Gibbs-preserving, i.e., $\Phi(\hat{\gamma}_\beta) = \hat{\gamma}_\beta$. The ergotropy of the final state $\Phi(\hat{\rho})$ is upper-bounded as*

$$R(\Phi(\hat{\rho})) \leq \frac{1}{\beta} S(\hat{\rho}\|\hat{\gamma}_\beta). \tag{4.26}$$

Proof. The corollary can be proven based on two key properties of the relative entropy and Gibbs-preserving map. Firstly, the non-negativity of the relative entropy, as well as the monotonicity of the relative entropy under Gibbs-preserving maps, which are given by the following inequalities:

$$\begin{aligned} \frac{1}{\beta} S(\Phi(\rho)_P\|\gamma\beta) &\geq 0, & (4.27)\\ \frac{1}{\beta}\left(S(\rho\|\gamma_\beta) - S(\Phi(\rho)\|\gamma_\beta)\right) &\geq 0, & (4.28) \end{aligned}$$

By substituting these inequalities into Eq. (4.23), we obtain the bound. □

The inequality given in Eq. (4.26) indicates that the amount of ergotropy extracted from the system cannot exceed the initial thermodynamic resource, which is determined by the non-equilibrium free energy. This result is consistent with the bound obtained in Eq. (4.13) [79], that is derived from a model that defines work in terms of changes in the average energy of a weight. Importantly, when there are no quantum correlations between the ideal weight and the system, the ergotropy can be related to the maximum change in the average energy of the weight. In such a scenario, the bound in Eq. (4.26) can be seen as another formulation of the second law of thermodynamics. This result can be extended to encompass ergotropy extraction for non-passive initial states through Gibbs-preserving maps.

Theorem 36 (Ultimate bound on extraction of ergotropy)**.** *The change of the ergotropy of the state ρ evolving via a Gibbs preserving map Φ (i.e. satisfying $\Phi(\gamma_\beta) = \gamma_\beta$) is upper bounded as*

$$R(\Phi(\rho)) - R(\rho) \leq \frac{1}{\beta} S(\rho_P\|\gamma_\beta). \tag{4.29}$$

Proof. We begin by writing the change in ergotropy using Eq. (4.16) as

$$\begin{aligned} R(\Phi(\rho)) - R(\rho) &= \Big(F(\Phi(\rho)) - F(\Phi(\rho)_P)\Big) - \Big(F(\rho) - F(\rho_P)\Big) \\ &= \Big(F(\rho_P) - F(\Phi(\rho)_P)\Big) - \Big(F(\rho) - F(\Phi(\rho))\Big) \\ &\leq \Big(F(\rho_P) - F(\Phi(\rho)_P)\Big) = \Big(F(\rho_P) - F(\gamma_\beta) + F(\gamma_\beta) - F(\Phi(\rho)_P)\Big) \\ &= \frac{1}{\beta}\Big(S(\rho_P\|\gamma_\beta) - S(\Phi(\rho)_P\|\gamma_\beta)\Big) \leq \frac{1}{\beta}S(\rho_P\|\gamma_\beta), \end{aligned} \tag{4.30}$$

where the initial inequality can be deduced from the fact that the free energy is monotonically non-increasing under the Gibbs-preserving map as given in Eq. (4.28), while the subsequent inequality can be obtained from the non-negative nature of the relative entropy Eq. (4.27). □

It is worth noting that the upper bound given in Eq. (4.29) does not rely on a specific Gibbs-preserving map Φ, but instead only depends on the initial state ρ. This bound is in agreement with the previously derived bound in Eq. (4.26), since $S(\rho_P\|\gamma_\beta) \leq S(\rho\|\gamma_\beta)$. When the initial state ρ is already passive, meaning $R(\rho) = 0$, then the inequality in Eq. (4.29) reduces to Eq. (4.26). Therefore, Eq. (4.29) can be interpreted as the *second law for ergotropy extraction* that places an upper limit on the amount of ergotropy that can be extracted through a Gibbs-preserving transformation.

In the next section, we shall construct an example that illustrates how the bound given in Eq. (4.29) can be saturated for a thermal operation.

4.6.1 The maximal-energy thermal process and saturation of the bound on ergotropy extraction

In this section, we present an example of a system that exists in the ground energy state of a Harmonic oscillator and transforms a thermal operation Φ_{max}, where the limit given in Eq. (4.29) is saturated. As the ground state of the Hamiltonian is energy incoherent, we shall employ theorem 22 to characterize this transformation. As per the theorem 22, transforming an energy-incoherent state through a thermal operation is equivalent to transforming the classical state constructed from it's diagonal via a Gibbs stochastic matrix. Thus, we will construct the Gibbs stochastic matrix $T^{\Phi_{\text{max}}}$ corresponding to the thermal operation Φ_{max}.

Consider a system in the ground state of a harmonic oscillator system described by Hamiltonian $H = \sum_{n=0}^{\infty} n\omega|n\rangle\langle n|$ (we re-scaled the ground state energy of the harmonic oscillator to zero and all the other energies accordingly). Then the classical state $\boldsymbol{g}$ constructed from diagonal of ground energy state $|0\rangle\langle 0$ transforms via the Gibbs stochastic matrix $T^{\Phi_{max}}$ which is as follows:

$$T^{\Phi_{\max}} = \begin{pmatrix} X & Y \\ \Omega & \mathbf{0} \end{pmatrix}, \tag{4.31}$$

where

$$X := \begin{pmatrix} 0 & 0 & 0 & 0 & \dots & 0 \\ 0 & 1 & 0 & 0 & \dots & 0 \\ 0 & 0 & 1 & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \dots & 1 \end{pmatrix}_{(L-1)\times(L-1)} \qquad Y := \begin{pmatrix} 1 & 1 & 1 & 1 & \dots & \dots \\ 0 & 0 & 0 & 0 & \dots & \dots \\ 0 & 0 & 0 & 0 & \dots & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \dots & \dots \end{pmatrix}_{(L-1)\times\infty} \tag{4.32}$$

$$\Omega := \frac{1}{Z}\begin{pmatrix} 1 & 0 & 0 & 0 & \dots & 0 \\ e^{-\beta\omega} & 0 & 0 & 0 & \dots & 0 \\ e^{-2\beta\omega} & 0 & 0 & 0 & \dots & 0 \\ e^{-3\beta\omega} & 0 & 0 & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \dots & \vdots \end{pmatrix}_{\infty\times(L-1)} \qquad \mathbf{0} := \begin{pmatrix} 0 & 0 & 0 & 0 & \dots & \dots \\ 0 & 0 & 0 & 0 & \dots & \dots \\ 0 & 0 & 0 & 0 & \dots & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \dots & \dots \end{pmatrix}_{\infty\times\infty} \tag{4.33}$$

such that

$$L = 1 + \frac{1}{\beta\omega}\log Z, \tag{4.34}$$

that takes integer values for $\frac{1}{\beta\omega}\log Z \in \mathbb{N}$, where $Z = \mathrm{Tr}(e^{-\beta H})$. It can be seen immediately that $T^{\Phi_{\max}}$ is stochastic, and that it preserves the classical state $\boldsymbol{\gamma}_\beta$ arises from the diagonal of the Gibbs state i.e.,

$$\boldsymbol{\gamma}_\beta = \Big(\frac{1}{Z} \quad \frac{e^{-\beta\omega}}{Z} \quad \frac{e^{-2\beta\omega}}{Z} \dots\Big)^T. \tag{4.35}$$

The action of $T^{\Phi_{\max}}$ on the classical state $\boldsymbol{g} = (1\ 0 \dots 0)^T$ characterizes the transformation of the ground state $|0\rangle\langle 0|$ as follows:

$$\Phi_{\text{max}}\Big(|0\rangle\langle 0|\Big) = G = \frac{1}{Z}\sum_{n=L}^{\infty} e^{-\beta\omega(n-L)}|n\rangle\langle n|. \tag{4.36}$$

It is worth noting that we can obtain $\Phi_{\text{max}}(|0\rangle\langle 0|)$ by placing $T^{\Phi_{\max}}\boldsymbol{g}$ on the diagonal component as $|0\rangle\langle 0|$ is energy incoherent. We observe that final state G is the Gibbs state γ_β, with populations displaced by ωL. To compute the ergotropy of the final state, we must first determine the corresponding passive state $\hat{G}_P$, which is the minimal energy state acquired by exchanging occupation probabilities. In the case of this infinite-dimensional system, the passive state is found as the limit where all *zeroes* occupying the first L energy levels are "pushed to infinity" (as in the Hilbert's Hotel paradox). In this scenario, we obtain $G_P = \gamma_\beta$, implying that the passive version of the final state $\hat{G}$ is the Gibbs state. However, this tech-

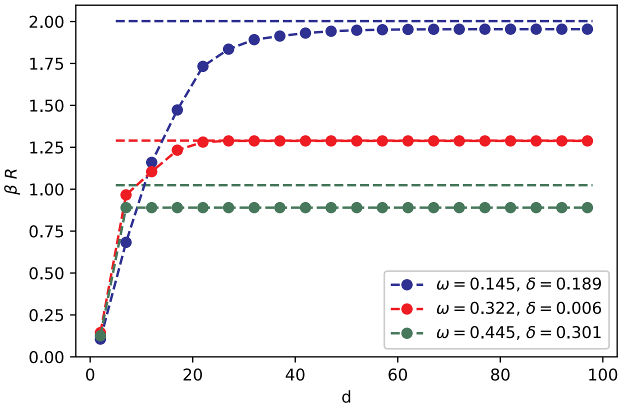

Figure 4.1: Consider the d-dimensional qudit with frequency ω, initially in the ground state, subjected to a thermal process at temperature β that maximizes the final energy. The dashed horizontal lines signify the ergotropy extraction bound given in Eq. (4.29). As the dimensionality of the qudit increases, it becomes evident that the final ergotropy for the maximal-energy process reaches saturation and approaches the optimal ergotropy as $\delta \to 0$.

nique for generating the passive state is not applicable in finite dimension, as the Gibbs state γ_β in such instances does not contain any *zeroes* within its spectrum.

Putting $G_P = \gamma_\beta$ turns the LHS of the inequality in Eq. (4.29) to

$$R(G) - R(|0\rangle\langle 0|) = E(G) - E(G_P) = E(G) - E(\gamma_\beta) = \frac{1}{\beta}\log Z, \tag{4.37}$$

while the RHS of the inequality is equal to:

$$\frac{1}{\beta} S(|0\rangle\langle 0|\|\hat{\gamma}_\beta) = \frac{1}{\beta}\log Z. \tag{4.38}$$

In the case where the harmonic oscillator possesses frequency ω and is in its ground state at zero temperature, such that $\frac{1}{\beta\omega}\log Z \in \mathbb{N}$, the ergotropy extraction bound presented in Eq. (4.29) reaches its maximum limit. The thermal process that achieves this saturation maximizes the final energy state. This maximization is evident from the fact that the first column of the Gibbs stochastic matrix $T^{\Phi_{\max}}$ acting on the ground state $|0\rangle\langle 0|$ entirely determines the transformation. The corresponding matrix element for the n-th row of the first column of Ω is upper bounded by $e^{-\beta\omega(L+n-2)}$, since it must be Gibbs-preserving, i.e., $T^{\Phi_{\max}}\gamma_\beta = \gamma_\beta$. It can be demonstrated, however, that this element is equivalent to $\frac{e^{-\beta\omega(n-1)}}{Z} = e^{-\beta\omega(L+n-2)}$ using Eq. 4.34. Therefore, the process maximizes the occupation of high energy states while reducing that of the lowest $L-1$ energy levels.

Finally, we conclude this chapter by providing a numerical study about the saturation of the bound on ergotropy extraction in Eq. (4.29) with dimensionality. In order to do so, we introduce the detuning parameter as follows:

$$\delta = \min\left[\frac{1}{\beta\omega}\log Z - \lfloor\frac{1}{\beta\omega}\log Z\rfloor, \lceil\frac{1}{\beta\omega}\log Z\rceil - \frac{1}{\beta\omega}\log Z\right]. \tag{4.39}$$

The numerical results of the final ergotropy for the d-dimensional system are presented in Fig. 4.1, with varying frequencies ω, and non-zero values of the detuning parameter δ. The ergotropy extraction protocol aims to maximize the energy of the final state. As δ approaches zero, the extractable ergotropy approaches the bound, even for moderate dimension d, while non-zero detuning parameter prohibits strict saturation, even in the infinite-dimensional limit. It is worth noting that as β approaches zero, thermal processes become permutations, and the protocol that maximizes the energy of the final state also maximizes its ergotropy. Therefore, the numerical outcomes in Fig. 4.1 imply that, for high bath temperatures and a harmonic oscillator initially in the ground state, no thermal operation can strictly saturate the bound Eq. (4.29) for non-zero detuning δ. In the following chapter, we shall elaborate on the ergotropy extraction in the finite dimensional scenario and describe the working of a microscopic heat engine using the tools of thermomajorization.

4.7 Conclusions and Outlook

This chapter introduces a bound on ergotropy extraction and demonstrates its achievability for infinite dimensional systems. However, for finite dimensional systems, there exists a discrepancy between the bound and actual extractable ergotropy. To advance our understanding of ergotropy extraction, we aim to investigate the role of coherence in the process by identifying a state σ satisfying $R(\sigma)-R(\rho) > R(\mathcal{D}(\sigma))-R(\mathcal{D}(\rho))$, which would provide a quantum advantage for ergotropy extraction and lead to higher work yields per cycle than classical engines. Additionally, the relationship between extractable ergotropy, optimized for all energy conserving operations, and the dimension of the working body is an open question. Fig. 4.1 illustrates this relationship for a qudit system initialized in the ground state and transformed by a thermal operation that extracts the maximum energy from the bath. The bound given in Eq. (4.18) characterizes the ergotropy of a composite system in the asymptotic limit of copies, with the Gibbs state serving as a completely passive state. Moreover, investigating the extractable ergotropy for composite systems coupled with a heat bath will provide insights into how emerging entanglement affects the extractable ergotropy. Finally, exploring the possibility of saturating the bound on ergotropy extraction for finite-dimensional systems using a catalyst is another avenue worth exploring, which will be discussed in the next chapter.

Chapter 5

Microscopic heat engine

5.1 Introduction

In this chapter, we will explore the consequences of the finite size of the system on the performance of microscopic heat engines. These engines have garnered significant interest in recent years, owing to their potential applications in diverse fields, such as information processing [79, 84, 148], sensing [149, 150, 151, 152], and energy conversion [153]. A microscopic heat engine is a thermodynamic device that operates at a microscopic level, converting heat energy into work. It comprises a working body, which can be a molecule, atom, or a single electron, and a heat source and sink [79, 154, 155]. The small size of the working body means that the operation of microscopic heat engines is governed by quantum mechanics, and their behaviour can vary substantially from their macroscopic counterparts. Research on microscopic heat engines has focused on investigating their thermodynamic efficiency and work production, as well as their limitations and potential applications. This research is crucial in advancing our understanding of the fundamental laws of thermodynamics at the nanoscale [79, 87, 146]. There are two main categories of microscopic heat engines based on their operation:

1. *Stroke-based engines*: These engines work by interacting with the heat baths, and work storage via energy-conserving strokes in a specific sequence.
2. *Self-contained engines*: All components of these engines undergo a transformation that conserves the engine's total energy.

The designs of the two engines differ fundamentally. The stroke-based engines assume the existence of an external control that regulates the sequence of strokes, while self-contained engines require no such external control for their performance. In this chapter, we will explore both open-cycle engines, which are stroke-based engines, and self-contained engines at the smallest possible size. We will develop a thermodynamic framework for both engines and analyze their performance in terms of work production and efficiency. Regarding self-contained engines, we will demonstrate how their performance can be enhanced by utilizing a catalyst. Moreover, we will investigate how to model such self-contained engines as autonomous heat engines using the Markovian master equation. We will begin by examining the functioning of the open-cycle engine that involves extracting ergotropy from a hot heat bath and storing it as work in the work storage during subsequent strokes.

5.2 The open-cycle heat engines

In this section, we will delve into the concept of an open-cycle heat engine, which is a stroke-based engine. We will explore the role of extracting ergotropy from the bath as work that can be stored in an ideal weight battery model presented in section 4.3 [79, 139]. Our investigation will focus on identifying the optimal performance of this engine and determining the states in which maximum work production and efficiency can be achieved. We will concentrate on open cycle engines that resemble the minimal coupling engines introduced in [146], which work by alternately coupling to the heat baths and the battery, much like traditional stroke-based engines. To describe the workings of open-cycle engines, we must first introduce a few concepts related to the thermal operation, which we will do in the following subsection.

5.2.1 Mathematical interlude

In subsection 2.3.2 of chapter 2, we have defined thermal operation as a CPTP map $\mathcal{E}$ that transforms the state of the system ρ_S as

$$\mathcal{E}(\rho_S) = \mathrm{Tr}_B\Big(U(\rho_S \otimes \tau)U^\dagger\Big) \tag{5.1}$$

where U satisfies the relation $[U, H_S + H_B] = 0$ with H_S, H_B are Hamiltonian of the system and the bath, and $\tau = \frac{e^{-\beta H_B}}{\mathrm{Tr}(e^{-\beta H_B})}$ is the thermal state of the bath.

If ρ_S is energy incoherent i.e. $[\rho_S, H_S] = 0$, one can characterize the transformation ρ_S under thermal operation $\mathcal{E}$ via the action of a Gibbs stochastic matrix $T^{\mathcal{E}}$ on the classical state $\boldsymbol{p}_S$ that is generated from the diagonal of ρ_S (see theorem 22). Therefore, $\mathcal{E}(\rho_S)$ can be constructed by placing the elements of $T^{\mathcal{E}}\boldsymbol{p}_S$ on the diagonal i.e.,

$$\mathcal{E}(\rho_S) = \sum_{i=1}^{d} \left(T^{\mathcal{E}}\boldsymbol{p}_S\right)_i |E_i\rangle\langle E_i|. \tag{5.2}$$

Employing the Blackwell's theorem (see theorem 11) we can say transformation of an energy incoherent states ρ_S via a thermal operation $\mathcal{E}$ can be characterized utilizing thermomajorization as follows:

$$\rho_S \to \mathcal{E}(\rho_S) \quad \Rightarrow \quad (\boldsymbol{p}_s, \boldsymbol{\gamma}_S) \succ (\boldsymbol{q}_s, \boldsymbol{\gamma}_S), \tag{5.3}$$

where $\boldsymbol{q}_S$ is the classical state constructed from the diagonal of $\mathcal{E}(\rho_S)$ and $\boldsymbol{\gamma}_S$ is the classical state generated from the diagonal of the Gibbs state of the system $\gamma_S = \frac{e^{-\beta H_S}}{\text{Tr}(e^{-\beta H_S})}$. Conversely, if $(\boldsymbol{p}_s, \boldsymbol{\gamma}_S) \succ (\boldsymbol{q}_s, \boldsymbol{\gamma}_S)$ then one can construct a Gibbs stochastic matrix T

$$T\boldsymbol{p}_S = \boldsymbol{q}_S \quad ; \quad T\boldsymbol{\gamma}_S = \boldsymbol{\gamma}_S. \tag{5.4}$$

This stochastic matrix T can generate a thermal operation $\mathcal{E}$ such that ρ_S transforms to $\mathcal{E}(\rho_S)$ that has $\boldsymbol{q}_S$ on the diagonal. we put 0 on the off-diagonals, since initial state ρ_S is energy incoherent and coherence can not be generated via a thermal operation as can be seen from proposition 26.

The future thermal cone $\mathcal{T}(\rho_S)$ (introduced in definition 25) for the energy incoherent state ρ_S includes all states that can be obtained from ρ_S through thermal operations. Since the set of thermal operations is convex (as per theorem 23), the future thermal cone of ρ_S is also convex. It can also be described as the set of classical states obtained from $\boldsymbol{p}_S$ via transformation by Gibbs stochastic matrices. To determine the extremal points of $\mathcal{T}(\rho_S)$, the concept of tight thermomajorization (introduced in [82, 156]) must be employed. We briefly describe the idea of tight thermomajorization here that involves the concepts of relative Lorenz curve introduced in definition 15.

Definition 34 (Tight thermomajorization)**.** If all extremal points (or elbows) of the thermomajorization curve of $L_{\boldsymbol{\gamma}_S}(\boldsymbol{q}_S)$ lies on the curve $L_{\boldsymbol{\gamma}_S}(\boldsymbol{p}_S)$, then $\boldsymbol{p}_S$ tightly thermomajorizes $\boldsymbol{q}_S$. Here $\boldsymbol{\gamma}_S$ denotes the classical state constructed from the diagonal of Gibbs state of the system and by extremal points of the curve we mean those points that can not be written as the convex sum of points that lies on the curve.

Lemma 37 (Characterizing the extremal points of $\mathcal{T}(\rho)$ (Theorem 4 of [156]))**.** *Consider a pair of energy incoherent state ρ_S and σ_S with the classical state generated from their diagonal $\boldsymbol{p}_S$ and $\boldsymbol{q}_S$. Then σ_S is the extremal point of the future thermal cone $\mathcal{T}(\rho_S)$ if and only if $\boldsymbol{p}_S$ tightly thermo-majorizes $\boldsymbol{q}_S$.*

Lastly, we introduce the concept of β-ordering before concluding this section.

Definition 35 (β- ordering)**.** Consider a pair of classical states $(\boldsymbol{p}_S, \boldsymbol{\gamma}_S)$ where $\boldsymbol{p}_S$ is the classical state generated from the diagonal of ρ_S and $\boldsymbol{\gamma}_S$ is the classical state generated from the diagonal of the Gibbs state of the system $\frac{e^{-\beta H_S}}{\text{Tr}(e^{-\beta H_S})}$ with Hamiltonian H_S at inverse temper-

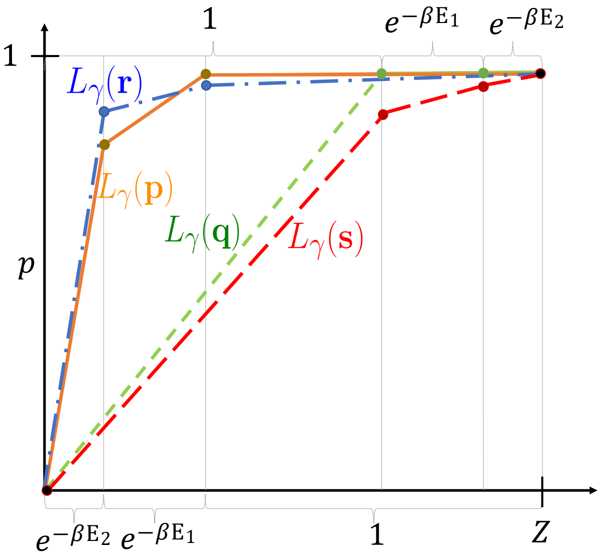

Figure 5.1: The *rescaled thermomajorization diagram* illustrates a three-dimensional system with Hamiltonian $H = E_1|E_1\rangle\langle E_1| + E_2|E_2\rangle\langle E_2|$, where $E_2 > E_1$. The X-axis is rescaled to Z, and the elbows of the curves are marked by circles. The curves $L_\gamma(\boldsymbol{s})$ and $L_\gamma(\boldsymbol{q})$ are *thermomajorized* by the curve $L_\gamma(\boldsymbol{p})$, while the curve $L_\gamma(\boldsymbol{p})$ does not thermomajorize $L_\gamma(\boldsymbol{r})$, nor does $L_\gamma(\boldsymbol{r})$ thermomajorize $L_\gamma(\boldsymbol{p})$. The curve $L_\gamma(\boldsymbol{q})$ is *tightly thermomajorized* by the curve $L_\gamma(\boldsymbol{p})$. The classical state $\boldsymbol{p}$ and $\boldsymbol{r}$ have β-order $(3, 2, 1)$, while $\boldsymbol{s}$ and $\boldsymbol{q}$ have β-order $(1, 2, 3)$.

ature β. We define the β- order as the ordering $\big(\pi(1)\ \pi(2)\ \ldots\ \pi(d)\big)$ such that

$$\frac{(\boldsymbol{p}_S)_{\pi(1)}}{(\boldsymbol{\gamma}_S)_{\pi(1)}} \geq \frac{(\boldsymbol{p}_S)_{\pi(2)}}{(\boldsymbol{\gamma}_S)_{\pi(2)}} \geq \ldots \geq \frac{(\boldsymbol{p}_S)_{\pi(d)}}{(\boldsymbol{\gamma}_S)_{\pi(d)}} \tag{5.5}$$

where π is a permutation acting on the set of indices $(1 \ldots d)$.

To understand the concepts of tight thermo-majorization and β-ordering more clearly, see the Fig. 5.1 where we plot the thermomajorization diagram for three dimensional classical state. The concept of β-ordering will be crucial to optimize the efficiency and work produced by the engine as well as to formulate the second law for open cycle engines. We shall see this shortly. In the next section, we shall describe the open-cycle engine in detail.

5.2.2 Description of the open cycle heat engine

The open cycle engine is composed of two baths, with inverse temperatures denoted as β_H and β_C, and a battery. The hot bath has an inverse temperature of β_H, while the cold bath has an inverse temperature of β_C, where β_H is less than β_C. Initially, the working body is in thermal equilibrium with the cold bath. During successive discrete two-body energy-

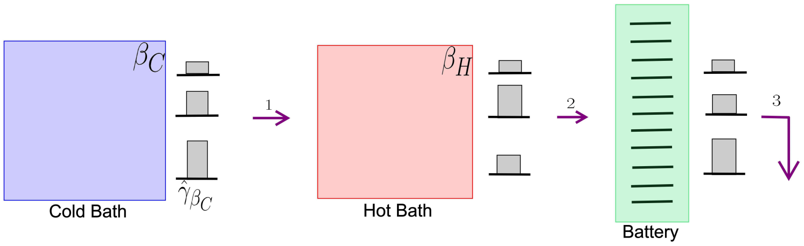

Figure 5.2: This diagram illustrates an open-cycle heat engine that uses a qutrit as its working body. The engine consists of two baths - a cold bath with inverse temperature β_C and a hot bath with inverse temperature β_H - as well as a battery that serves as a work storage. Initially, the working medium is in thermal equilibrium with the cold bath. In stroke 1, the working body extracts ergotropy from the hot bath, causing it to become non-passive. In stroke 2, the ergotropy is stored as work in the battery, resulting in a passive state for the working body. Finally, in stroke 3, the working body can either be discarded or returned to thermal equilibrium with the cold bath.

conserving operations, referred to as *strokes*, the working body couples alternately with the hot bath and battery. The Fig. 5.2 presents a schematic representation of the design for an open-cycle engine with a qutrit working body. Similarly to the minimal coupling quantum heat engines introduced in [145], this engine uses the interaction between the hot bath and the working body in its initial stroke to extract ergotropy. This extracted ergotropy is then stored as work on the battery in the second stroke. Finally, the working body is thermalized with the cold bath or discarded in the last stroke. A detailed description of the engine follows.

5.2.2.1 Working body thermalized with respect to cold bath.

To start the process, we initialize both of the baths in equilibrium i.e.,

$$\tau_{\beta_H} = \frac{e^{-\beta_H H_H}}{\mathrm{Tr}(e^{-\beta_H H_H})} \quad ; \quad \tau_{\beta_C} = \frac{e^{-\beta_C H_C}}{\mathrm{Tr}(e^{-\beta_C H_C})} \tag{5.6}$$

where H_H and H_C are Hamiltonians of the hot and cold baths, respectively. It is assumed that the heat capacities of the baths are infinite, which guarantees that their temperatures remain stable during the engine's operation. The working body is a d-dimensional system that is initially in thermal equilibrium with the cold bath. The Hamiltonian that describes the working body, can be expressed as follows:

$$H_S = \sum_{i=0}^{d} \omega_i |\epsilon_i\rangle\langle\epsilon_i|, \tag{5.7}$$

with the state of the working body is expressed as:

$$\rho_S = \frac{e^{-\beta_C H_S}}{\mathrm{Tr}(e^{-\beta_C H_S})}. \tag{5.8}$$

Assuming the components of the engine are initially uncorrelated, the initial state of the engine can be written as

$$\rho = \rho_S \otimes \tau_{\beta_H} \otimes \rho_B, \tag{5.9}$$

where ρ_B is a state of the battery. The free Hamiltonian H_0 of the combined system is given by

$$H_0 = H_S + H_H + H_B, \tag{5.10}$$

where H_S, H_H and H_B are Hamiltonian of the system, hot bath, and battery respectively. When the open-cycle engine runs repeatedly, it stores the ergotropy of the working body to the battery and then thermalizes it again with a cold bath. As a result, the engine is only influenced by the change in the state of the battery ρ_B at the start of each run. The role of the working body is to direct the energy flow from the hot bath to the battery, as outlined below.

5.2.2.2 Interaction of working body with the hot heat bath and battery via discrete two body energy conserving strokes.

According to the definition of stroke operations in [145], we restrict interactions to occur only between two bodies at a time. As a result, the unitary evolution of an engine can be represented as the product of two unitaries:

$$U = U_B U_H, \tag{5.11}$$

where U_H corresponds to the interaction between the working body and the hot bath, and U_B corresponds to the interaction between the system and the battery.

To ensure energy conservation in the engine, we require that the unitaries preserve the total energy. Thus, we apply the condition

$$[U_H, H_S + H_H] = 0; \quad \text{and} \quad ; [U_B, H_S + H_B] = 0. \tag{5.12}$$

The purpose of utilizing unitary U_H is to extract ergotropy from the hot bath and transfer it to the working body during the first stroke. Similarly, the unitary U_B is used to charge the battery by converting the extracted ergotropy into work during the second stroke. Hence, the sequence of unitaries specified in Eq. (5.11) is appropriate.

The unitary U_H describes the interaction between the working body and the hot bath, and it can also be expressed as a thermal operation $\mathcal{E}_H$ that transforms the state ρ_S. Specifically, $\mathcal{E}_H$ allows for the extraction of ergotropy from the hot bath by converting the initial state ρ_S into a new state $\mathcal{E}_H(\rho_S)$, where τ_H is the thermal state of the hot bath. Mathematically, this transformation can be represented as follows:

$$\rho_S \to \mathcal{E}_H(\rho_S) = \mathrm{Tr}_H[U_H(\rho_S \otimes \tau_H)U_H^\dagger], \tag{5.13}$$

Since the initial state of the working body ρ_S is Gibbs with respect to the cold bath, as given in Eq. (5.8), the value of the thermodynamic resource $R(\rho_S)$ is zero. Therefore, according to the ideal weight model presented in section 4.3 as the work storage, the amount of work stored during the second stroke is equal to the ergotropy obtained during the first stroke, as shown in [79, 145]:

$$W(\mathcal{E}_H(\rho_S)) = R(\mathcal{E}_H(\rho_S)). \tag{5.14}$$

During the interaction of the working body with the hot bath, heat is transferred from the hot bath to the working body, leading to an increase in the system's average energy. The amount of heat transferred, denoted as Q, is defined as the change in the system's average energy due to its interaction with the hot bath, which can be expressed as:

$$Q(\mathcal{E}_H(\rho_S)) = \mathrm{Tr}[(H_S(\mathcal{E}_H(\rho_S) - \rho_S)], \tag{5.15}$$

where $\mathcal{E}_H(\rho_S)$ represents the state of the working body after interacting with the hot bath, and H_S is the Hamiltonian of the system.

Clausius's formulation of the second law of thermodynamics states that, without an external work source, heat will always flow from a hotter object to a colder one. This concept is reflected in the Eq. (5.15) which ensures that the amount of heat transferred is non-negative:

Lemma 38 (Directionality of heat flow from hot bath to a working body that is thermalized with cold bath)**.** *Suppose we have a state ρ_S that has been initially thermalized with a cold bath at temperature β_C. If we subject the state ρ_S to any thermal operation $\mathcal{E}_H$ in the presence of a hot bath at temperature β_H, the amount of heat exchanged during the process can be determined using Eq. (5.15). This quantity, denoted by $Q(\mathcal{E}_H(\rho_S))$, is always non-negative, as expressed by the inequality:*

$$Tr(H_S(\mathcal{E}_H(\rho_S) - \rho_S)) \geq 0. \tag{5.16}$$

Proof sketch: By exploiting the linearity of the function $Q(\mathcal{E}_H(\rho_S))$, we can establish that the minimum amount of heat transferred occurs at one of the extremal points in the set $\mathcal{T}(\rho_S)$, that comprises the states achievable by applying a thermal operation on ρ_S. Among these extremal points, the state ρ_S itself is one such point. To prove that the average energy of

ρ_S is not surpassed by that of any other extremal points in $\mathcal{T}(\hat{\rho}_S)$, we first note that there is only one extremal element in this set with a β-order (for the definition of β-order, refer to section in the appendix) of $(1, 2, \ldots, d)$. We then demonstrate that for any state with a different β-order, there exists a thermal operation $\mathcal{A}$ that reduces its average energy. As a result, the average energy of any extremal states in $\mathcal{T}(\rho_S)$, except for ρ_S, is higher than the average energy of some other state in $\mathcal{T}(\rho_S)$ (i.e., the state obtained by applying $\mathcal{A}$). Hence, the minimum amount of heat transferred is attained at ρ_S, resulting in a value of Q equal to zero. The complete proof can be found in section 6.7 of the appendix.

☐

In an open-cycle heat engine, the efficiency can be defined as the ratio of the work stored in the battery to the heat exchanged from the hot bath. This can be represented using the equation:

$$\eta(\mathcal{E}_H(\rho_S)) = \frac{W(\mathcal{E}_H(\rho_S))}{Q(\mathcal{E}_H(\rho_S))} = \frac{R(\mathcal{E}_H(\rho_S))}{Q(\mathcal{E}_H(\rho_S))}. \tag{5.17}$$

The next section will cover the optimal performance of the open cycle heat engine, with a focus on maximizing the work stored in the battery while achieving the highest possible efficiency. This goal is synonymous with extracting the maximum ergotropy from the hot heat bath, as evidenced by Eq. (5.14).

5.2.3 Optimal performance for the open cycle heat engine

Our objective in this analysis is to maximize the work and efficiency, as defined in Eq. (5.14) and Eq. (5.17), respectively, for the set of states that can be obtained from the initial state of the working body, ρ_S, via thermal operations. Since it is clear from a referenced lemma 37 that the set of states achievable from any energy incoherent state using thermal operations also forms a polytope. We refer to this set as the thermal polytope of the state ρ_S, denoted as $\mathcal{T}(\rho_S)$. Our goal, therefore, is to maximize the work and efficiency over all the states within $\mathcal{T}(\rho_S)$, which can be expressed as:

$$W_{\text{max}} = \max_{\sigma_S \in \mathcal{T}(\rho_S)} R(\sigma_S) \quad ; \quad \eta_{\text{max}} = \max_{\sigma_S \in \mathcal{T}(\rho_S)} \eta(\sigma_S). \tag{5.18}$$

The theorem below characterises the states in the $\mathcal{T}(\rho_S)$ which lead to optimal work and efficiency.

Theorem 39 (Optimal work production of open cycle engine)**.** *The maximum possible values of work and efficiency for an open cycle quantum heat engine are achieved at the extremal points of the set $\mathcal{T}(\hat{\rho}_S)$.*

Proof. To optimize work production we need to maximize ergotropy function over the future thermal cone of ρ_S denoted by $\mathcal{T}(\rho_S)$ (see Eq. (5.18)). From the definition of ergotropy given in Eq. (4.11), we can prove the convexity for ergotropy as follows,

$$\begin{aligned}
R(\alpha\rho + (1-\alpha)\sigma) &= \max_{U \in \mathcal{U}(d)} \mathrm{Tr}\Big(H\big(\alpha\rho + (1-\alpha)\sigma - U(\alpha\rho + (1-\alpha)\sigma)U^{\dagger}\big)\Big) \\
&= \max_{U \in \mathcal{U}(d)} \mathrm{Tr}\Big(\big(\alpha H\big(\rho - U\rho U^{\dagger}\big) + (1-\alpha)H\big(\sigma - U\sigma U^{\dagger}\big)\Big) \\
&\leq \alpha \max_{U \in \mathcal{U}(d)} \mathrm{Tr}\big(H(\rho - U\rho U^{\dagger})\big) + (1-\alpha) \max_{U \in \mathcal{U}(d)} \mathrm{Tr}\big(H(\sigma - U\sigma U^{\dagger})\big) \\
&= \alpha R(\rho) + (1-\alpha)R(\sigma), \qquad (5.19)
\end{aligned}$$

where ρ and σ are any arbitrary states and $\alpha \in [0,1]$. Using the fact that maxima of convex function restricted over a polytope, obtained at the extremal points of the polytope. This implies that the maximum value of work production is achieved at an extremal point of $\mathcal{T}(\rho_S)$.

To maximize efficiency, we note that an arbitrary state $\sigma \in \mathcal{T}(\rho_S)$ can be written as $\sigma = \sum_i \lambda_i \sigma_i$, where $\{\sigma_i\}$ are extremal points of $\mathcal{T}(\rho_S)$ and $\lambda_i \in [0,1]$ for each i. Thus, one can write employing Eq. (5.14) and Eq. (5.17) the following

$$\begin{aligned}
\eta(\sigma) = \frac{R(\sigma)}{Q(\sigma)} = \frac{R(\sum_i \lambda_i \sigma_i)}{Q(\sum_i \lambda_i \sigma_i)} &\leq \frac{\sum_i \lambda_i R(\sigma_i)}{\sum_i \lambda_i Q(\sigma_i)} \qquad (5.20) \\
&= \sum_j \left(\frac{\lambda_j Q(\sigma_j)}{\sum_i \lambda_i Q(\sigma_i)}\right) \frac{R(\sigma_j)}{Q(\sigma_j)} \leq \max_j \frac{R(\sigma_j)}{Q(\sigma_j)} = \max_j \eta(\sigma_j),
\end{aligned}$$

where the first inequality exploits convexity of ergotropy and linearity of the function $Q(\cdot)$, and the second inequality uses lemma 38 that says $Q(\sigma_j)$ is non-negative for all extremal states, and therefore $\left(\frac{\lambda_j Q(\sigma_j)}{\sum_i \lambda_i Q(\sigma_i)}\right) \in [0,1]$. ☐

To optimize the work and efficiency of an open-cycle quantum heat engine, it is necessary to optimize over all the extremal points of $\mathcal{T}(\rho_S)$. It is important to note that achieving maximum values of both work and efficiency simultaneously may not be feasible. The upcoming sections will focus on analyzing the optimal performance of qubit and qutrit working bodies in an open cycle heat engine and exploring the process of ergotropy extraction in low-dimensional systems. To identify the extremal points of the set $\mathcal{T}(\rho_S)$, we will rely on the results presented in [157].

5.2.3.1 Open cycle heat engine with qubit working body

Let us examine a qubit working body ρ_S with a Hamiltonian of the form

$$\omega|1\rangle\langle 1|, \qquad (5.21)$$

which is in a thermal state at an inverse temperature β_C. This state can be expressed as:

$$\rho_S = \frac{1}{1+e^{-\beta_C \omega}} \begin{pmatrix} 1 & 0 \\ 0 & e^{-\beta_C \omega} \end{pmatrix}. \tag{5.22}$$

Using the idea of tight thermomajorization presented in lemma 37, one can easily characterize $\mathcal{T}(\rho_S)$ as convex hull with two extremal points as follows [33]:

$$\mathcal{T}(\rho_S) = \text{conv}\left\{ \rho_S \;,\; \frac{1}{1+e^{-\beta_C \omega}} \begin{pmatrix} 1+(e^{-\beta_C \omega} - e^{-\beta_H \omega}) & 0 \\ 0 & e^{-\beta_H \omega} \end{pmatrix} \right\}, \tag{5.23}$$

where ρ_S is given in Eq. (5.22). From theorem 39, we optimise the performance of open cycle heat engine over extremal points of $\mathcal{T}(\rho_S)$ as given in Eq. (5.23). Therefore, we evaluate work production and efficiency of the engine at

$$\frac{1}{1+e^{-\beta_C \omega}} \begin{pmatrix} 1+(e^{-\beta_C \omega} - e^{-\beta_H \omega}) & 0 \\ 0 & e^{-\beta_H \omega} \end{pmatrix}, \tag{5.24}$$

which is the only extremal point that results non-trivial work production and efficiency. We calculate the optimal work output defined in Eq. (5.14) as

$$W = \omega \Big(\frac{2e^{-\beta_H \omega}}{1+e^{-\beta_C \omega}} - 1 \Big). \tag{5.25}$$

Therefore, the engine leads to non-zero work production if and only if $2e^{-\beta_H \omega} - 1 > e^{-\beta_C \omega}$. In order to calculate the efficiency, we need to calculate the amount of heat exchanged given in Eq. (5.15) that can be expressed as

$$Q = \frac{\omega}{1+e^{-\beta_C \omega}} (e^{-\beta_H \omega} - e^{-\beta_C \omega}). \tag{5.26}$$

Therefore, the optimal efficiency is given by

$$\eta = 1 - \frac{(1-e^{-\beta_H \omega})}{(e^{-\beta_H \omega} - e^{-\beta_C \omega})}. \tag{5.27}$$

Let us now compare with the more general case of minimal coupling quantum heat engines from [145], for which we have

$$W_{\text{mc}} = \omega \Big(\frac{2e^{-\beta_H \omega}}{1+e^{-(\beta_C+\beta_H)\omega}} - 1 \Big), \tag{5.28}$$

$$\eta_{\text{mc}} = 1 - \frac{(1-e^{-\beta_H \omega})}{(e^{-\beta_H \omega} - e^{-(\beta_C+\beta_H)\omega})}. \tag{5.29}$$

Hence, we can conclude that $W_{\text{mc}} \geq W$ and $\eta_{\text{mc}} \geq \eta$, and equality is achieved when

$\beta_C \to \infty$. This outcome results from the understanding that open-cycle engines are minimal coupling engines, which means that the working body is restored to its initial state by thermalizing with the cold bath. Furthermore, by examining Eq. (5.25) and Eq. (5.28), we observe that minimal coupling heat engines can operate within a broader temperature range, allowing them to produce non-zero work over a wider range of temperatures. Moving on, our focus now shifts to the qutrit case of open-cycle heat engines, which has not been characterized for minimal coupling heat engines to the best of our knowledge.

5.2.3.2 Open cycle heat engine with a qutrit working body

We consider the working body as a qutrit with Hamiltonian

$$H_S = \omega_1 |1\rangle\langle 1| + \omega_2 |2\rangle\langle 2| \tag{5.30}$$

that is initialized in a thermal state given by

$$\rho_S = \frac{1}{1 + e^{-\beta_C \omega_1} + e^{-\beta_C \omega_2}} \begin{pmatrix} 1 & 0 & 0 \\ 0 & e^{-\beta_C \omega_1} & 0 \\ 0 & 0 & e^{-\beta_C \omega_2} \end{pmatrix}. \tag{5.31}$$

Employing theorem 39, to optimize the work production and efficiency of a heat engine, we consider all extremal points of the set $\mathcal{T}(\rho_S)$. In order to characterize the set $\mathcal{T}(\rho_S)$, we use lemma 1 from [157] that characterize the extremal points of $\mathcal{T}(\rho_S)$. We shall state this lemma using the following quantities q^H_{ij} and q^C_{ij} that are defined as follows:

$$\begin{aligned} q^H_{ij} &= e^{-\beta_H(\omega_i - \omega_j)}, & (5.32) \\ q^C_{ij} &= e^{-\beta_C(\omega_i - \omega_j)}, & (5.33) \end{aligned}$$

with $\omega_0 = 0$. We rewrite ρ_S given in Eq. (5.31) as

$$\rho_S = \frac{1}{\mathcal{Z}_C} \Big(|0\rangle\langle 0| + q^C_{10} |1\rangle\langle 1| + q^C_{20} |2\rangle\langle 2| \Big), \tag{5.34}$$

where $\mathcal{Z}_C = 1 + q^C_{10} + q^C_{20}$. The application of [157] (see lemma 2 of appendix for details) results in the following:

Lemma 1. *[Extremal points of the qutrit thermal polytope] The possible states that can be reached by thermal operation while in contact with a bath at inverse temperature β_H, starting from the initial state ρ_S as defined in Eq. (5.34), form a convex hull consisting of extremal points. The set of extremal points can be expressed as follows:*

$$\mathcal{T}(\rho_S) = \begin{cases} conv\,\{\rho_S \,,\, \rho^1_S \,,\, \rho^2_S \,,\, \rho^3_S \,,\, \rho^4_S\} & \text{for } \beta_H \geq \beta_0, \\ conv\,\{\rho_S \,,\, \rho^1_S \,,\, \rho^2_S \,,\, \rho^3_S \,,\, \rho^5_S \,,\, \rho^6_S\} & \text{for } \beta_H < \beta_0, \end{cases} \tag{5.35}$$

Here β_0 *is specified by the relation*

$$e^{-\beta_0\omega_1} + e^{-\beta_0\omega_2} = 1, \tag{5.36}$$

and extremal points are defined as

$$\rho_S^1 = \frac{1}{\mathcal{Z}_C}\Big((1 - q_{10}^H + q_{10}^C)|0\rangle\langle 0| + q_{10}^H|1\rangle\langle 1| + q_{20}^C|2\rangle\langle 2|\Big), \tag{5.37}$$

$$\rho_S^2 = \frac{1}{\mathcal{Z}_C}\Big((1|0\rangle\langle 0| + ((1 - q_{21}^H)q_{10}^C + q_{20}^C)|1\rangle\langle 1| + q_{21}^H q_{10}^C|2\rangle\langle 2|\Big), \tag{5.38}$$

$$\rho_S^3 = \frac{1}{\mathcal{Z}_C}\Big((1 - q_{20}^H + q_{21}^H q_{10}^C)|0\rangle\langle 0| + ((1 - q_{21}^H)q_{10}^C + q_{20}^C)|1\rangle\langle 1| + q_{20}^H|2\rangle\langle 2|\Big), \tag{5.39}$$

$$\rho_S^4 = \frac{1}{\mathcal{Z}_C}\Big((1 + q_{10}^C + q_{20}^C - q_{10}^H - q_{20}^H)|0\rangle\langle 0| + q_{10}^H|1\rangle\langle 1| + q_{20}^H|2\rangle\langle 2|\Big), \tag{5.40}$$

$$\hat{\rho}_S^5 = \frac{1}{\mathcal{Z}_C}\Big(((q_{01}^H - q_{21}^H)q_{10}^C + q_{20}^C)|0\rangle\langle 0| + q_{10}^H|1\rangle\langle 1| + (1 - q_{10}^H + (1 - q_{01}^H + q_{21}^H)q_{10}^C)|2\rangle\langle 2|\Big), \tag{5.41}$$

$$\rho_S^6 = \frac{1}{\mathcal{Z}_C}\Big((q_{10}^C(q_{01}^H - q_{21}^H) + q_{20}^C)|0\rangle\langle 0| + (1 - q_{20}^H + q_{10}^C(1 - q_{01}^H + q_{21}^H))|1\rangle\langle 1| + q_{20}^H|2\rangle\langle 2|\Big), \tag{5.42}$$

where $\mathcal{Z}_C = 1 + q_{10}^C + q_{20}^C$.

Optimizing the extremal points of $\mathcal{T}(\rho_S)$ poses a significant challenge as it relies on the values of β_H, ω_1, and ω_2. In order to determine the amount of work produced by the heat engine, we utilize Eq. (5.14) and examine the quantity of ergotropy obtained from the hot bath. The values for β_H, ω_1, and ω_2 are provided in table 5.1, while table 5.2 displays the heat exchanged with the hot bath for each extremal state. The efficiency of the heat engine can be computed by dividing the quantity of ergotropy extracted by the corresponding amount of heat exchanged.

We analyze numerically the optimal work production and efficiency for a qutrit Hamiltonian given by

$$H = |1\rangle\langle 1| + \omega|2\rangle\langle 2|. \tag{5.43}$$

We characterize the optimal protocols for work production, which can be identified by different states of the working body Eqs. (5.37)-(5.42) obtained by applying a thermal operation to the initial state (see Fig. 5.3). It is important to note that, unlike the infinite-dimensional that we investigate in chapter 4 for low-dimensional systems, the optimal protocols for extracting ergotropy may not maximize the energy of the working body.

Fig. 5.4 shows the values of extractable ergotropy and efficiency of the engine. We observe that the region where ergotropy can be extracted decreases as ω increases. When $\omega \to \infty$ and $\beta_C \to \infty$, the condition $\beta_H < \log 2$ is recovered, which limits the operational regime of a qubit minimal step engine [145]. For high values of ω, extremal Gibbs stochastic

Extremal states	Amount of ergotropy extracted
ρ_S^1	$\max\Big\{0, \frac{\omega_1}{Z_C}\Big(2q_{10}^H - 1 - q_{10}^C\Big)\Big\}$
ρ_S^2	$\max\Big\{0, \frac{1}{Z_C}(\omega_2 - \omega_1)\Big(2q_{21}^H q_{10}^C - (q_{10}^C + q_{20}^C\Big)\Big\}$
ρ_S^3	$\max\Big\{0, \frac{(\omega_2-\omega_1)}{Z_C}\Big(q_{20}^H - q_{20}^C - (1 - q_{21}^H)q_{10}^C\Big),\ \frac{\omega_2}{Z_C}q_{20}^H - \frac{\omega_1}{Z_C}\Big((1 - q_{20}^H) + q_{21}^H q_{10}^C\Big)$ $-\frac{(\omega_2-\omega_1)}{Z_C}\Big((1 - q_{21}^H)q_{10}^C + q_{20}^C\Big)\Big\}$
ρ_S^4	$\max\Big\{0,\ \frac{\omega_1}{Z_C}\Big(2q_{10}^H + q_{20}^H - (1 + q_{10}^C + q_{20}^C)\Big),\ \frac{\omega_1}{Z_C}(q_{10}^H - q_{20}^H) + \frac{\omega_2}{Z_C}\Big(2q_{20}^H + q_{10}^H$ $-(1 + q_{10}^C + q_{20}^C)\Big)\Big\}$
ρ_S^5	$\max\Big\{0, \frac{\omega_1}{Z_C}\Big(q_{10}^H - (q_{01}^H - q_{21}^H)q_{10}^C - q_{20}^C)\Big),\ \frac{\omega_1}{Z_C}\Big(q_{10}^H - (1 - q_{10}^H)$ $-(1 - q_{01}^H - q_{21}^H)q_{10}^C\Big) + \frac{\omega_2}{Z_C}\Big((1 - q_{10}^H) + (1 - q_{01}^H - q_{21}^H)q_{10}^C$ $-(q_{01}^H - q_{21}^H)q_{10}^C - q_{20}^C\Big)\Big\}$
ρ_S^6	$\max\Big\{0, \frac{\omega_2-\omega_1}{Z_C}\Big(2q_{20}^H - 1 - q_{10}^C(1 + q_{21}^H - q_{01}^H)\Big),\ \frac{\omega_1}{Z_C}\Big(1 - q_{20}^C - q_{20}^H$ $+q_{10}^C(1 + 2q_{21}^H - 2q_{01}^H)\Big),\ \frac{\omega_1}{Z_C}\Big(q_{10}^C(1 + q_{21}^H - q_{01}^H) + 1 - 2q_{20}^H\Big)$ $+\frac{\omega_2}{Z_C}\Big(q_{20}^H - q_{20}^C + q_{10}^C q_{21}^H - q_{10}^C q_{01}^H\Big), \frac{\omega_1}{Z_C}\Big(1 - q_{20}^C - q_{20}^H$ $+q_{10}^C(1 + 2q_{21}^H - 2q_{01}^H)\Big) - \frac{\omega_2}{Z_C}\Big(1 - 2q_{20}^H$ $+q_{10}^C(1 + q_{21}^H - q_{01}^H)\Big),\ \frac{\omega_2}{Z_C}\Big(q_{20}^H - q_{20}^C + q_{10}^C(q_{21}^H - q_{01}^H)\Big)\Big\}$

Table 5.1: The amount of ergotropy extracted from various extremal states, subject to different permutations.

Extremal states	Amount of Heat Exchanged
ρ_S^1	$\frac{1}{Z_C}\omega_1\Big(q_{10}^H - q_{10}^C\Big)$
ρ_S^2	$\frac{1}{Z_C}\Big(\omega_2 - \omega_1\Big)\Big(q_{10}^C(q_{21}^H - q_{21}^C)\Big)$
ρ_S^3	$\frac{1}{Z_C}\Big(q_{20}^H\omega_2 - q_{20}^C(\omega_2 - \omega_1) - q_{10}^C q_{21}^H\omega_1)\Big)$
ρ_S^4	$\frac{1}{Z_C}\Big((q_{10}^H - q_{10}^C)\omega_1 + (q_{20}^H - q_{20}^C)\omega_2\Big)$
ρ_S^5	$\frac{1}{Z_C}\Bigg(q_{10}^H(1 - q_{10}^C q_{01}^H)\omega_1 + \Big(q_{10}^C q_{20}^H q_{01}^H - q_{20}^C + (1 - q_{10}^C q_{01}^H)(1 - q_{10}^H)\Big)\omega_2\Bigg)$
ρ_S^6	$\frac{1}{Z_C}\Big(1 - q_{10}^C q_{01}^H)(1 - q_{20}^H)\omega_1 + (q_{20}^H - q_{20}^C)\omega_2\Big)$

Table 5.2: The amount of heat exchanged from various extremal states, subject to different permutations.

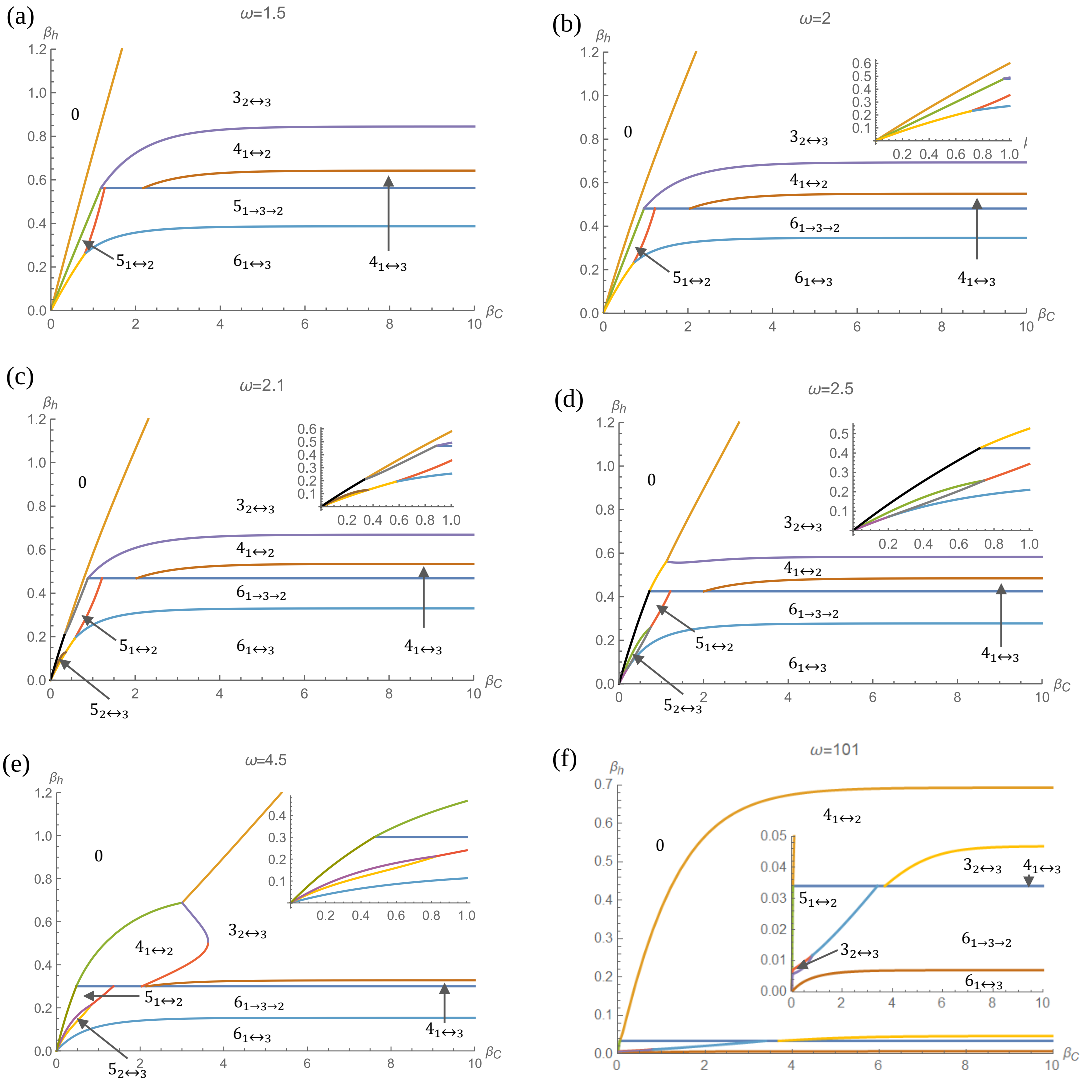

Figure 5.3: **Protocols for optimal ergotropy extraction:** This diagram represents optimal protocols for extracting ergotropy from a qutrit Gibbs state with an inverse temperature of β_C, interacting with a thermal bath with an inverse temperature of β_H and a Hamiltonian spectrum of $(0, 1, \omega)$. The values of ω considered are: (a) 1.5, (b) 2, (c) 2.1, (d) 2.5, (e) 4.5, and (f) 101. The region in which ergotropy extraction is not possible is represented by 0. Other regions are marked by symbols corresponding to the optimal final states, as described by Eqs. (5.37)-(5.42), along with the subscripts indicating the permutation leading to optimal ergotropy extraction. A transition between protocols 4 and 5 or 4 and 6 occurs at the point where $1 = e^{-\beta_H} + e^{-\beta_H \omega}$.

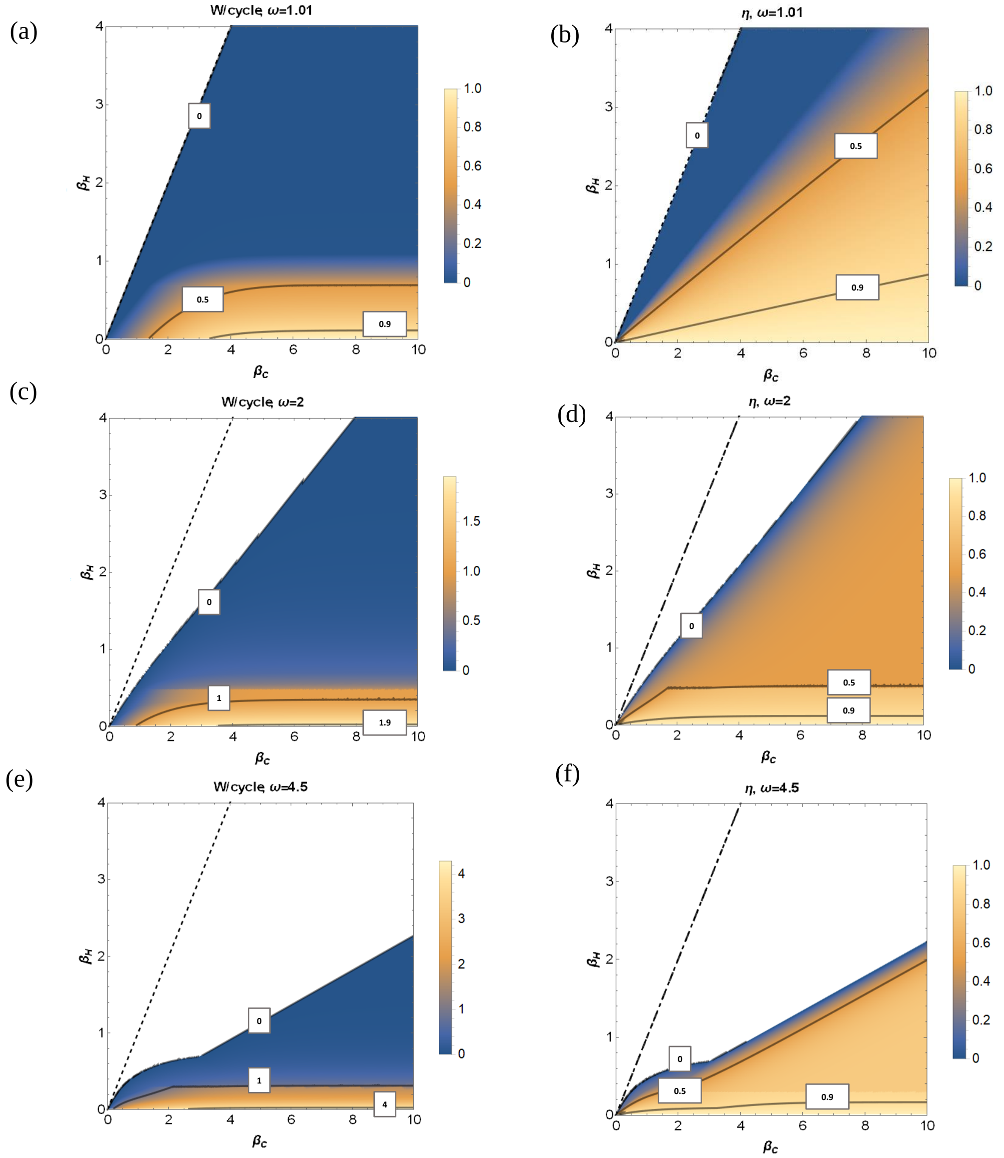

Figure 5.4: This diagram represents the work production per cycle and efficiencies of the open-cycle engine for different qutrit spectra, as shown in panels (a) and (b) for $\omega = 1.01$, panels (c) and (d) for $\omega = 2$, and panels (e) and (f) for $\omega = 4.5$. The dashed line in each panel represents the operational region in the limit as ω approaches 1.

matrices acting on a qutrit Gibbs state cannot result in higher population inversion than those acting on a qubit system (see section 6.8 of the appendix).

The optimal process for maximizing energy is achieved by a process that leads to the state ρ_S^6 when the limit $\beta_H \to 0$. However, when β_H is not equal to zero, the landscape of optimal protocols becomes very complex. Specifically, when β_H approaches critical values that satisfy $1 = e^{-\beta_H} + e^{-\beta_H \omega}$, the efficiency and extracted work may strongly depend on β_H. This can be attributed to the different structures of the set of extremal Gibbs stochastic matrices above and below this limit, as explained in [157]. We anticipate that the diversity of optimal strategies will increase with the dimension of the working body.

5.2.3.3 Open cycle heat engine with qudit working body

In the preceding section, we demonstrated that non-passive state configurations become increasingly complex when transitioning from two-level to three-level systems. Therefore, to accurately characterize d-dimensional qudits, we conducted a numerical simulation to determine optimal work production and efficiency. Our method for computing optimal quantities relied on thermomajorization. We used a numerical search to identify all extremal points within the set $\mathcal{T}(\rho_S)$ for a given initial state ρ_S. Fig. 5.5 shows the results. However, since the number of extremal points in a thermal polytope increase in factorial order with dimension, we could not perform these computations for moderate $d > 8$. Nevertheless, optimization across all possible protocols for ergotropy extraction suggests that both work production and efficiency increase in tandem with the dimension of the working body, although the bound in Eq. (4.29) cannot be fully saturated for small dimensions. These findings are similar to those obtained for a limited class of protocols designed to optimize energy (see Fig. 4.1) and are consistent with the idea that a low-dimensional working body requires a careful optimization process because it enforces a separation (in terms of relative entropy) between the Gibbs state and the state resulting from ergotropy extraction, thus preventing the saturation of the bound.

In the next section we shall focus on the self-contained heat engine.

5.3 Self-contained heat engine

To operate a stroke-based heat engine, discrete stages of external driving are required to regulate its operation. It's crucial that during the working process, the working body interacts with a specific subsystem without interference from others. For example, when the working body engages with the hot bath, it can't simultaneously interact with the work storage or cold bath, and the same applies to later interactions. While it's theoretically possible to design such external driving, implementing it experimentally poses a challenge. Further-

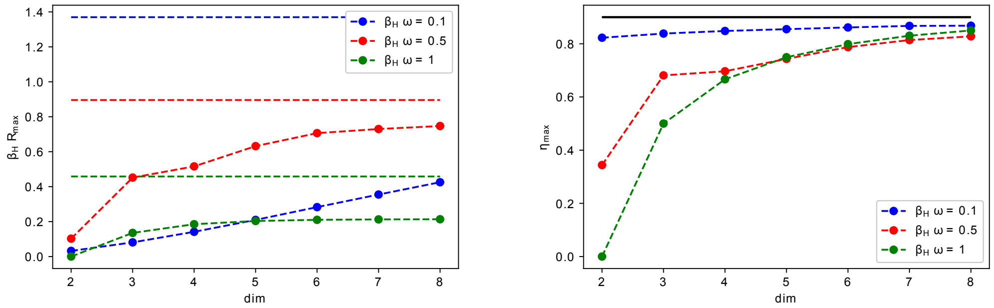

Figure 5.5: The diagram represents the work production and efficiency of an open-cycle engine with a d-dimensional working body having a constant energy gap of ω. The plots were generated using a fixed initial Gibbs state at a cold (inverse) temperature of $\beta_C\omega = 10$ and for different values of $\beta_H\omega$. The left panel shows the work production, which is represented by the optimal extracted ergotropy $\beta_H R_{max}$. The dashed horizontal lines correspond to the free energy bound as described in Eq. (4.29). The right panel displays the efficiency of the ergotropy extraction process as defined in Eq. (5.17). The black solid line represents the Carnot efficiency for $\beta_C/\beta_H = 10$.

more, the assumption that external driving doesn't consume energy in minimal coupling engines is incorrect. This provides motivation for exploring self-contained heat engines that don't need external control [154, 158].

5.3.1 Description of self-contained heat engine

The heat engine comprises of two d-level systems that are in equilibrium with separate heat baths. The first d-level system is referred to as the *hot* d- level system or hot qudit and is characterized by the Hamiltonian H_H. It is connected to a heat bath with an inverse temperature β_H. The second d-level system is known as the *cold* d- level system or cold qudit and is described by Hamiltonian H_C. It is connected to a heat bath with an inverse temperature β_C, where $\beta_C > \beta_H$, which justifies their names. Additionally, the engine contains work storage or battery that is modelled using a translationally invariant weight, as discussed in section 4.3.

A self-contained heat engine differs from stroke-based heat engines in that it undergoes a single, global energy-conserving operation that transforms all of its components, rather than operating in discrete steps. The name self-contained is justified by this operation, as it does not require an external control to run the engine as shown in Fig. 5.7. Additionally, a working body component called a *catalyst* can assist the self-contained engine in such a way that the marginal state of the catalyst is preserved at the end of the global energy-conserving operation, thus closing the cycle. We refer to such an engine as a *catalyst-assisted self-contained engine*. Similarly, it is possible to miniaturize a self-contained engine without the catalyst as shown in Fig. 5.6. One of the aims of this chapter is to demonstrate

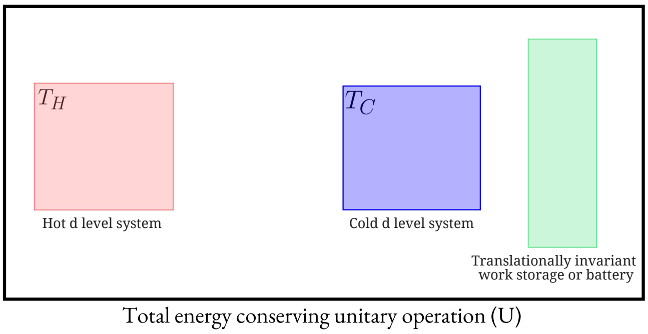

Figure 5.6: **Schematic representation of a self-contained heat engine without a catalyst:** This diagram depicts the construction and operation of a self-contained heat engine. The engine comprises hot and cold d-level systems at temperatures T_H and T_C, respectively, where $T_H > T_C$. Work storage or *battery* is modelled using a translationally invariant weight, as introduced in section 4.3. The total state of the engine is transformed by a unitary that preserves the total energy of the engine, such that $[U, H_H + H_C + H_W] = 0$. In order to extract work, we would like to choose U in such a way that the average energy of the work storage increases.

that incorporating a catalyst leads to the enhancement of the performance of quantum heat engines.

The aim of this engine is to increase the average energy of the work storage system after the global energy-conserving operation. This increase is called *work*, while the decrease in the average energy of the hot qudit is referred to as *heat*. The efficiency of the heat engine is calculated by determining the ratio of work and heat. In the next section, we formulate the concept of work and heat more rigorously.

5.3.2 Thermodynamical framework for self-contained heat engine without catalyst

In the start, we assume that all the components of the engines are uncorrelated with hot and cold d-level systems are thermalized at inverse temperature β_H and β_C, respectively. Therefore, the initial state of the engine is given by $\tau^{\mathrm{i}}_{HCW} := \tau_{\beta_H} \otimes \tau_{\beta_C} \otimes \rho_W$ where

$$\tau_{\beta_H} = \frac{e^{-\beta_H H_H}}{\mathrm{Tr}(e^{-\beta_H H_H})} \quad ; \quad \tau_{\beta_C} = \frac{e^{-\beta_C H_C}}{\mathrm{Tr}(e^{-\beta_C H_C})}, \tag{5.44}$$

with β_i and H_i is the inverse temperature and Hamiltonian of i^{th} d-level system with $i \in \{H, C\}$ and ρ_W is the state of the work storage described by Hamiltonian H_W (see in definition 29 and discussion after that). The combined state of the d-level hot and cold system, as well as the work storage will be denoted as τ^{f}_{HCW}. For the self-contained engine, the presence of the external work source or control is not required, and all possible energy expenditures need to be tracked. Therefore, we assume that the transformation from τ^{i}_{HCW} to

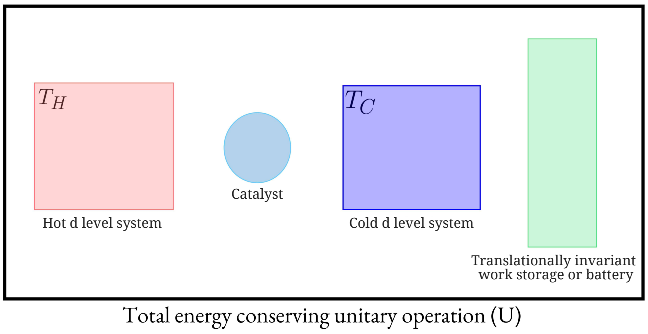

Figure 5.7: **Schematic representation of a self-contained heat engine with a catalyst:** This diagram depicts the construction and operation of a self-contained heat engine that is aided by a catalyst. The engine comprises hot and cold d-level systems at temperatures T_H and T_C, respectively, where $T_H > T_C$. Work storage or *battery* is modelled using a translationally invariant weight, as introduced in section 4.3. Furthermore, the self-contained heat engine is aided by a catalyst whose marginal state is preserved after the transformation. The total state of the engine is transformed by a unitary that preserves the total energy of the engine, such that $[U, H_S + H_H + H_C + H_W] = 0$. In order to extract work, we would like to choose U in such a way that the average energy of the work storage increases.

τ^{f}_{HCW} occurs through a unitary operation denoted as U, which conserves the total energy of the engine, i.e.,

$$\tau^{\mathrm{f}}_{HCW} = U\tau^{\mathrm{i}}_{HCW}U^{\dagger} \quad \text{where} \quad [U, H_H + H_C + H_W] = 0. \tag{5.45}$$

This ensures that the total energy of the engine is conserved during the transformation.

The work performed by the engine corresponds to the increase in the average energy of the weight, as expressed by the following equation:

$$W = \mathrm{Tr}\Big(H_W(\tau^{\mathrm{f}}_{HCW} - \tau^{\mathrm{i}}_{HCW})\Big). \tag{5.46}$$

We assume that this work is independent of the initial state of the work storage, which means that the unitary U commutes with the generator of the translation operator that shifts the energy spectrum of the work storage (refer to section 4.3 of chapter 4). Using the condition $[U, H_H + H_C + H_W] = 0$, we can rewrite the expression for the work performed by the engine as follows:

$$W = \mathrm{Tr}\Big((H_H + H_C)(\tau^{\mathrm{i}}_{HC} - \tau^{\mathrm{f}}_{HC})\Big), \tag{5.47}$$

where τ^{i}_{HC} and τ^{f}_{HC} represent the initial and final states of the d-level hot and cold system. This equation basically tells that the drop of energy by the hot and cold qudit will be stored as work in the battery. The formula given in Eq. (5.47) will make it simpler to analyse work production as well as the efficiency of the engine.

The lemma 33 from chapter 4 allows us to infer that $\tau^{\mathrm{f}}_{HC} = V\tau^{\mathrm{i}}_{HC}V^{\dagger}$, where V is a unitary operator that acts on the hot and cold d-level system. Therefore, we obtain:

$$W = \mathrm{Tr}\Big((H_H + H_C)(\tau^{\mathrm{i}}_{HC} - V\tau^{\mathrm{f}}_{HC}V^{\dagger})\Big) = \mathrm{Tr}\Big((H_H + H_C)\big(\tau_{\beta_H}\otimes\tau_{\beta_C} - V(\tau_{\beta_H}\otimes\tau_{\beta_C})V^{\dagger}\big)\Big). \tag{5.48}$$

In order to characterize the amount of heat exchanged we consider the drop of energy of the hot d level system. The amount of heat exchanged from the hot heat bath is given by

$$Q_H = \mathrm{Tr}\Big(H_H \mathrm{Tr}_{CW}\Big(\tau^{\mathrm{i}}_{HCW} - \tau^{\mathrm{f}}_{HCW}\Big)\Big) = \mathrm{Tr}\Big(H_H\big(\tau_{\beta_H} - \mathrm{Tr}_C(\tau^{\mathrm{f}}_{HC})\big)\Big). \tag{5.49}$$

Therefore, the efficiency of the engine is given by η where

$$\eta = \frac{W}{Q_H}. \tag{5.50}$$

Now we shall provide two equivalent formulations of the second law in this setting. In order to do so we need the concepts of entropy non-decreasing transformations which are a more generic set of transformations that contains any unitary operations.

Definition 36 (Entropy non-decreasing transformation). An entropy non-increasing transformation $\mathcal{U}$ is a CPTP map acting on on the set of d-dimensional density matrices $\mathcal{S}(\mathcal{H}_d)$ such that

$$\rho \xrightarrow{\mathcal{U}} \sigma, \tag{5.51}$$

that satisfies $S(\rho) \leq S(\sigma)$ where $S(\,\cdot\,)$ denotes the von Neumann entropy.

Using the idea of entropy non-decreasing transformation, we shall formulate the second law for the self contained heat engine without a catalyst which is in parallel to the Planck's statement of second law of thermodynamics.

Lemma 40 (Positivity of work done implies positivity of heat exchange)**.** *For any entropy non-decreasing transformation $\mathcal{U}$ such that $\mathcal{U}(\tau^{i}_{HC}) = \tau^{f}_{HC}$ where $\tau^{i}_{HC} = \tau_{\beta_H}\otimes\tau_{\beta_C}$ given in Eq.* (5.44) *the following relation holds:*

$$W > 0 \Rightarrow Q_H > 0. \tag{5.52}$$

Proof. From the definition of work done by the engine given in Eq. (5.46) we have

$$\begin{aligned} W &= \mathrm{Tr}\Big((H_H + H_C)(\tau^{\mathrm{i}}_{HC} - \tau^{\mathrm{f}}_{HC})\Big) = \mathrm{Tr}\Big(H_H(\tau^{\mathrm{i}}_{HC} - \tau^{\mathrm{f}}_{HC})\Big) + \mathrm{Tr}\Big(H_C(\tau^{\mathrm{i}}_{HC} - \tau^{\mathrm{f}}_{HC})\Big) \\ &= \mathrm{Tr}\Big(H_H\mathrm{Tr}_C\Big(\tau^{\mathrm{i}}_{HC} - \tau^{\mathrm{f}}_{HC}\Big)\Big) + \mathrm{Tr}\Big(H_C\mathrm{Tr}_H\Big(\tau^{\mathrm{i}}_{HC} - \tau^{\mathrm{f}}_{HC}\Big)\Big) = Q_H + Q_C, \end{aligned} \tag{5.53}$$

where $Q_C = \mathrm{Tr}\Big(H_C\mathrm{Tr}_H\Big(\tau^{\mathrm{i}}_{HC} - \tau^{\mathrm{f}}_{HC}\Big)\Big)$ can be understood as the amount heat dumped into the cold heat bath. Therefore,

$$W > 0 \quad \Rightarrow \quad Q_H + Q_C > 0. \tag{5.54}$$

From entropy decreasing property of the transformation $\mathcal{U}$ we have, $S(\tau^{f}_{HC}) = S(\tau^{i}_{HC}) + \delta$ for some $\delta \geq 0$ Moreover, employing the non-negativity of relative entropy we have the following:

$$D(\tau^{\mathrm{f}}_{HC} \| \tau^{\mathrm{i}}_{HC}) \geq 0, \tag{5.55}$$

implies

$$\begin{aligned} D(\tau^{\mathrm{f}}_{HC} \| \tau^{\mathrm{i}}_{HC}) &= -S(\tau^{\mathrm{f}}_{HC}) - \mathrm{Tr}(\tau^{\mathrm{f}}_{HC} \log \tau^{\mathrm{i}}_{HC}) = -S(\tau^{\mathrm{i}}_{HC}) - \mathrm{Tr}(\tau^{\mathrm{f}}_{HC} \log \tau^{\mathrm{i}}_{HC}) - \delta \\ &= \mathrm{Tr}\Big((\tau^{\mathrm{i}}_{HC} - \tau^{\mathrm{f}}_{HC}) \log \tau^{\mathrm{i}}_{HC}\Big) - \delta \\ &= \mathrm{Tr}\Big((\tau^{\mathrm{i}}_{HC} - \tau^{\mathrm{f}}_{HC})(-\beta_H H_H - \beta_C H_C)\Big) - \delta \\ &= -(\beta_H Q_H + \beta_C Q_C) - \delta \geq 0. \end{aligned} \tag{5.56}$$

From Eq. (5.56) we have $-(\beta_H Q_H + \beta_C Q_C) \geq \delta \geq 0$. Thus we can provide the following bound on Q_C

$$-\frac{\beta_H}{\beta_C} Q_H \geq Q_C. \tag{5.57}$$

Thus, combining with Eq. (5.54) we have

$$\begin{aligned} Q_H + Q_C > 0 \quad &\Rightarrow \quad Q_H\Big(1 - \frac{\beta_H}{\beta_C}\Big) > 0 \\ &\Rightarrow \quad Q_H > 0, \end{aligned} \tag{5.58}$$

since $\beta_C > \beta_H$. This completes the proof. □

Note that from Eq. (5.56) we immediately see

$$\eta = \frac{Q_H + Q_C}{Q_H} = 1 - \frac{\beta_H}{\beta_C} - \frac{D(\tau^{\mathrm{f}}_{HC} \| \tau^{\mathrm{i}}_{HC})}{\beta_C Q_H} < 1 - \frac{\beta_H}{\beta_C} := \eta_C. \tag{5.59}$$

So, from this lemma, we conclude that if the engine produces a positive amount of work, it implies that the engine had consumed a positive amount of heat and its efficiency is upper bounded by Carnot efficiency. This will allow us to formulate the second law in another way in terms of the efficiency of the process that will be stated in the following proposition.

Proposition 41. *Consider entropy non-decreasing transformations $\mathcal{U}_1$ and $\mathcal{U}_2$ acting on $\tau^{i}_{HC} = \tau_{\beta_H} \otimes \tau_{\beta_C}$ where τ_{β_H} and τ_{β_C} given in Eq. (5.44), with $\mathcal{U}_1(\tau^{i}_{HC}) = \tau^{1}_{HC}$ and $\mathcal{U}_2(\tau^{i}_{HC}) = \tau^{2}_{HC}$ such* *that*

$$\begin{aligned} W_1 &= Tr\Big((H_H + H_C)(\tau^i_{HC} - \tau^1_{HC})\Big) > 0 \\ W_2 &= Tr\Big((H_H + H_C)(\tau^i_{HC} - \tau^2_{HC})\Big) < 0 \\ Q_2 &= Tr\Big(H_H Tr_C\Big(\tau^i_{HC} - \tau^2_{HC}\Big)\Big) < 0. \end{aligned} \tag{5.60}$$

Then the following inequality holds:

$$\eta_1 := \frac{W_1}{Q_1} \leq \frac{W_2}{Q_2} := \eta_2, \tag{5.61}$$

where $Q_1 = Tr\Big(H_H Tr_C\Big(\tau^i_{HC} - \tau^1_{HC}\Big)\Big)$.

Proof. We shall proof this result using contradiction argument. Note that from lemma 40 we have $Q_1 > 0$. We proceed by assuming $\eta_1 > \eta_2$ that implies

$$\frac{W_1}{Q_1} > \frac{W_2}{Q_2} \quad \Rightarrow \quad W_1 Q_2 < W_2 Q_1, \tag{5.62}$$

where we obtain the RHS of '⇒' by multiplying the negative term $Q_1 Q_2$ on both side of $\frac{W_1}{Q_1} > \frac{W_2}{Q_2}$. Consider the following entropy non-increasing transformation $\mathcal{U}$

$$\mathcal{U} = \frac{-Q_2}{Q_1 - Q_2}\mathcal{U}_1 + \frac{Q_1}{Q_1 - Q_2}\mathcal{U}_2, \tag{5.63}$$

acting on τ^{i}_{HC}. From the linearity of the function $W(\cdot)$ and $Q(\cdot)$, we calculate work done and the amount of heat exchanged from the hot bath for such a transformation as follows:

$$W_{\mathcal{U}} = \mathrm{Tr}\Big((H_H + H_C)\Big(\tau^{\mathrm{i}}_{HC} - \mathcal{U}(\tau^i_{HC})\Big)\Big) = \frac{1}{Q_1 - Q_2}\Big(Q_1 W_2 - Q_2 W_1\Big) > 0, \tag{5.64}$$

$$Q_{\mathcal{U}} = \mathrm{Tr}\Big(H_H \mathrm{Tr}_C\Big(\tau^{\mathrm{i}}_{HC} - \mathcal{U}(\tau^i_{HC})\Big)\Big) = \frac{1}{Q_1 - Q_2}\Big(Q_1 Q_2 - Q_2 Q_1\Big) = 0. \tag{5.65}$$

This result clearly contradicts with lemma 40 that says for any entropy non-increasing transformation positivity of work implies positive amount of heat exchanged from the hot heat bath. This implies $\eta_1 > \eta_2$ can not be true which completes the proof. □

Optimizing the work production is straightforward as the maximum work that can be produced by such an engine is given by ergotropy. In the next section, we would proceed to optimize the efficiency of the self-contained heat engine without a catalyst.

5.3.2.1 Optimal efficiency of the self-contained heat engine without a catalyst

In order to optimize the efficiency, we shall show that among all the unitaries that can act on τ_{β_H} and τ_{β_C}, only permutation can lead to the optimal efficiency.

Theorem 42. *The optimal efficiency of self contained heat engine is achieved when the initial state of the hot and cold d- level system $\tau^i_{HC} = \tau_{\beta_H} \otimes \tau_{\beta_C}$ evolves via a permutation that results a positive amount of work.*

Proof. In order to demonstrate the assertion, our approach involves linking a d-dimensional vector $|A\rangle$ to the $d \times d$ matrix A expressed in the eigenbasis of the Hamiltonian $H_H + H_C$, which is denoted as $|E_i\rangle$ in the following manner:

$$\begin{aligned} &\text{Given } A = \sum_{ij} \langle E_i|A|E_j\rangle |E_i\rangle\langle E_j|, \\ \Rightarrow \qquad &|A\rangle = (\langle E_1|A|E_1\rangle, \dots, \langle E_d|A|E_d\rangle)^T. \end{aligned} \tag{5.66}$$

Then we can associate the vector $|H\rangle$, $|H_H\rangle$ and $|H_C\rangle$ with total Hamiltonian H, hot and cold bath Hamiltonian H_H and H_C respectively, in above mentioned manner as:

$$\begin{aligned} |H\rangle &= |\mathrm{Eig}(H_H)\rangle \otimes |\mathbb{1}\rangle + |\mathbb{1}\rangle \otimes |\mathrm{Eig}(H_C)\rangle, \\ |H_H\rangle &= |\mathrm{Eig}(H_H)\rangle \otimes |\mathbb{1}\rangle, \\ |H_C\rangle &= |\mathbb{1}\rangle \otimes |\mathrm{Eig}(H_C)\rangle, \end{aligned} \tag{5.67}$$

with

$$|\mathrm{Eig}(H_H)\rangle = (E^H_1 \; E^H_2 \; \dots E^H_d)^T, \quad |\mathrm{Eig}(H_C)\rangle = (E^C_1 \; E^C_2 \; \dots E^C_d)^T, \quad |\mathbb{1}\rangle = (1\;1\;\dots 1)^T. \tag{5.68}$$

Note that initial state $\tau_{\beta_H} \otimes \tau_{\beta_C}$ is diagonal in the energy eigenbasis and the final state of the engine is given by $U(\tau_{\beta_H} \otimes \tau_{\beta_C})U^\dagger$ where U is unitary. We know from Birkhoff's theorem [14] that eigenvalue of a hermitian matrix majorizes it's diagonal part. Thus, it implies

$$|\mathrm{Eig}(U(\tau_{\beta_H} \otimes \tau_{\beta_C})U^\dagger)\rangle \succ |U(\tau_{\beta_H} \otimes \tau_{\beta_C})U^\dagger\rangle, \tag{5.69}$$

where $|\mathrm{Eig}(\,\cdot\,)\rangle$ denotes the vector of eigenvalues and $|\cdot\rangle$ denotes the vector of diagonal elements. Since applying unitary does not change the spectrum (it can only permute the eigenvalues), thus we can write

$$|\mathrm{Eig}(U(\tau_{\beta_H} \otimes \tau_{\beta_C})U^\dagger)\rangle = \Pi|\mathrm{Eig}(\tau_{\beta_H} \otimes \tau_{\beta_C})\rangle = |\tau_{\beta_H} \otimes \tau_{\beta_C}\rangle, \tag{5.70}$$

where Π is a permutation, we write the final equality based on the fact initial state $\tau_{\beta_H} \otimes \tau_{\beta_C}$ is diagonal in the energy eigenbasis. Thus Eq. (5.69) boils down to

$$|\mathrm{Eig}(U(\tau_{\beta_H} \otimes \tau_{\beta_C})U^\dagger)\rangle = \Pi|\mathrm{Eig}(\tau_{\beta_H} \otimes \tau_{\beta_C})\rangle = |\tau_{\beta_H} \otimes \tau_{\beta_C}\rangle \succ |U(\tau_{\beta_H} \otimes \tau_{\beta_C})U^\dagger\rangle. \tag{5.71}$$

As $|\tau_{\beta_H} \otimes \tau_{\beta_C}\rangle = |\tau^{\mathrm{i}}_{HC}\rangle$ and $|U(\tau_{\beta_H} \otimes \tau_{\beta_C})U^\dagger\rangle = |\tau^{\mathrm{f}}_{HC}\rangle$, employing theorem 9 from chapter

1, we can write

$$|\tau^{\mathrm{f}}_{HC}\rangle = B|\tau^{\mathrm{i}}_{HC}\rangle \tag{5.72}$$

where B is a bistochastic matrix. Thus the amount of work done by the engine and the amount of heat exchanged is given by

$$W = \langle H|\tau^{\mathrm{i}}_{HC}\rangle - \langle H|B|\tau^{\mathrm{i}}_{HC}\rangle \quad ; \quad Q = \langle H_H|\tau^{\mathrm{i}}_{HC}\rangle - \langle H_H|B|\tau^{\mathrm{i}}_{HC}\rangle. \tag{5.73}$$

Therefore, we can write efficiency η as

$$\begin{aligned}
\eta &= \frac{\langle H|\tau^{\mathrm{i}}_{HC}\rangle - \langle H|B|\tau^{\mathrm{i}}_{HC}\rangle}{\langle H_H|\tau^{\mathrm{i}}_{HC}\rangle - \langle H_H|B|\tau^{\mathrm{i}}_{HC}\rangle} = \frac{\langle H|\tau^{\mathrm{i}}_{HC}\rangle - \langle H|(\sum_i \lambda_i \Pi_i)|\tau^{\mathrm{i}}_{HC}\rangle}{\langle H_H|\tau^{\mathrm{i}}_{HC}\rangle - \langle H_H|(\sum_i \lambda_i \Pi_i)|\tau^{\mathrm{i}}_{HC}\rangle}, \\
&= \sum_j \frac{\lambda_j(\langle H_H|\tau^{\mathrm{i}}_{HC}\rangle - \langle H_H|\Pi_j|\tau^{\mathrm{i}}_{HC}\rangle)}{\sum_i \lambda_i(\langle H_H|\tau^{\mathrm{i}}_{HC}\rangle - \langle H_H|\Pi_i|\tau^{\mathrm{i}}_{HC}\rangle)} \times \frac{(\langle H|\tau^{\mathrm{i}}_{HC}\rangle - \langle H|\Pi_j|\tau^{\mathrm{i}}_{HC}\rangle)}{(\langle H_H|\tau^{\mathrm{i}}_{HC}\rangle - \langle H_H|\Pi_j|\tau^{\mathrm{i}}_{HC}\rangle)}, \\
&= \sum_j \frac{\lambda_j Q_{\Pi_j}}{Q_H}\frac{W_{\Pi_j}}{Q_{\Pi_j}} = \sum_j \frac{\lambda_j Q_{\Pi_j}}{Q_H}\eta_{\Pi_j}.
\end{aligned} \tag{5.74}$$

where we write the second equality using Bikhoff-von Neumann theorem (as proven in section 6.1 of the appendix). Note that Q_{Π_j} are non-zero real numbers and $\lambda_j \in [0,1]\ \forall j$ such that $\sum_j \frac{\lambda_j Q_{\Pi_j}}{Q_H} = 1$. We can distinguish the summands appeared in Eq. (5.74) into three regime.

1. $\mathcal{J}_E := \{j : \quad \frac{\lambda_j Q_{\Pi_j}}{Q_H} > 0 \ , \ \eta_{\Pi_j} > 0\}$.
2. $\mathcal{J}_H := \{j : \quad \frac{\lambda_j Q_{\Pi_j}}{Q_H} > 0 \ , \ \eta_{\Pi_j} < 0\}$.
3. $\mathcal{J}_C := \{j : \quad \frac{\lambda_j Q_{\Pi_j}}{Q_H} < 0 \ , \ \eta_{\Pi_j} > 0\}$.

Note that existence of j such that $\frac{\lambda_j Q_{\Pi_j}}{Q_H} < 0$ and $\eta_{\Pi_j} < 0$ satisfies simultaneously, is not possible since the existence of such a process will leads to positive work done with a negative amount of heat exchanged with the hot reservoir. This is not allowed by the second law as given in lemma 40. Let us define $\eta^E_{\Pi^*}$ as the maximum efficiency in the redime $\mathcal{J}_E$ i.e.,

$$\eta^E_{\Pi^*} := \max_{j\in\mathcal{J}_E} \eta_{\Pi_j}. \tag{5.75}$$

Then

$$\sum_{j\in\mathcal{J}_E} \frac{\lambda_j Q_{\Pi_j}}{Q_H}\eta_{\Pi_j} \leq \sum_{j\in\mathcal{J}_E} \frac{\lambda_j Q_{\Pi_j}}{Q_H}\eta^E_{\Pi^*}. \tag{5.76}$$

It is also obvious to see that

$$\sum_{j\in\mathcal{J}_H} \frac{\lambda_j Q_{\Pi_j}}{Q_H}\eta_{\Pi_j} \leq \sum_{j\in\mathcal{J}_H} \frac{\lambda_j Q_{\Pi_j}}{Q_H}\eta^E_{\Pi^*}, \tag{5.77}$$

as for all $j \in \mathcal{J}_H$ we have $\eta_{\Pi_j} < 0$. Furthermore, employing proposition 41 and invoking the fact that $\frac{\lambda_j Q_{\Pi_j}}{Q_H}\eta_{\Pi_j} < 0$ for $j \in \mathcal{J}_C$, we can write

$$\begin{aligned} &\forall j \in \mathcal{J}_C, \quad \eta_{\Pi_j} > \eta_{\Pi^*}, \\ &\sum_{j\in\mathcal{J}_C} \frac{\lambda_j Q_{\Pi_j}}{Q_H}\eta_{\Pi_j} \leq \sum_{j\in\mathcal{J}_C} \frac{\lambda_j Q_{\Pi_j}}{Q_H}\eta^E_{\Pi^*}. \end{aligned} \tag{5.78}$$

Now, we can provide the bound on η as follows:

$$\begin{aligned} \eta &= \sum_j \frac{\lambda_j Q_{\Pi_j}}{Q_H}\eta_{\Pi_j} = \sum_{j\in\mathcal{J}_E} \frac{\lambda_j Q_{\Pi_j}}{Q_H}\eta_{\Pi_j} + \sum_{j\in\mathcal{J}_H} \frac{\lambda_j Q_{\Pi_j}}{Q_H}\eta_{\Pi_j} + \sum_{j\in\mathcal{J}_C} \frac{\lambda_j Q_{\Pi_j}}{Q_H}\eta_{\Pi_j}, \\ &\leq \eta^E_{\Pi^*}\left(\sum_j \frac{\lambda_j Q_{\Pi_j}}{Q_H}\right) = \eta^E_{\Pi^*}. \end{aligned} \tag{5.79}$$

This completes the proof. □

Since the number of permutations grows very fast with the increase of the size of the engine, this optimization problem gets quickly intractable. But, since we are dealing with a microscopic heat engine, we shall employ the above theorem to find the optimal efficiency of the engine where hot and cold systems are qubit. This is the smallest possible self-contained heat engine introduced in [154].

5.3.2.2 Smallest possible heat engine

In this section, we shall analyze the performance of the smallest possible autonomous heat engine where the hot and cold d level systems are qubit. The the hot and cold baths are in equilibrium w.r.t. Hamiltonian $H_H = \omega_H|1\rangle\langle 1|$ and $H_C = \omega_C|1\rangle\langle 1|$ and inverse temperature β_H and β_C. Therefore, the combined state of hot and the cold bath is given as

$$\begin{aligned} |\tau^i_{HC}\rangle &= \frac{1}{1+a_H}(1 \ \ a_H)^T \otimes \frac{1}{1+a_C}(1 \ \ a_C)^T, \\ &= \frac{1}{(1+a_H)(1+a_C)}(1 \ \ a_C \ \ a_H \ \ a_C a_H)^T. \end{aligned} \tag{5.80}$$

where $a_H = e^{-\beta_H\omega_H}$ and $a_C = e^{-\beta_C\omega_C}$. The total Hamiltonian is given as $H = H_H \otimes \mathbb{I} + \mathbb{I} \otimes H_C$, thus

$$|H\rangle = (0 \ \ \omega_C \ \ \omega_H \ \ \omega_C + \omega_H)^T \quad ; \quad |H_H\rangle = (0 \ \ 0 \ \ \omega_H \ \ \omega_H)^T. \tag{5.81}$$

From the initial state given in Eq. (5.80), we easily see that only one permutation Π leads to positive work that is given below:

$$\begin{aligned} |\tau^{\mathrm{i}}_{HC}\rangle &= \frac{1}{(1+a_H)(1+a_C)}(1 \;\; a_C \;\; a_H \;\; a_C a_H)^T, \\ &\xrightarrow{\Pi} \frac{1}{(1+a_H)(1+a_C)}(1 \;\; a_H \;\; a_C \;\; a_C a_H)^T := |\tau^{\mathrm{f}}_{HC}\rangle. \end{aligned} \tag{5.82}$$

Therefore, the optimal work production is given by

$$W = \mathrm{Tr}\Big(H(\tau^{\mathrm{i}}_{HC} - \tau^{\mathrm{f}}_{HC})\Big) = \langle H|\tau^{\mathrm{i}}_{HC}\rangle - \langle H|\tau^{\mathrm{f}}_{HC}\rangle = (a_H - a_C)(\omega_H - \omega_C). \tag{5.83}$$

Similarly, the amount of heat exchanged from the hot reservoir can be calculated as

$$Q = \mathrm{Tr}\Big(H_H \otimes \mathbb{I}(\tau^{\mathrm{i}}_{HC} - \tau^{\mathrm{f}}_{HC})\Big) = \langle H_H|\tau^{\mathrm{i}}_{HC}\rangle - \langle H_H|\tau^{\mathrm{f}}_{HC}\rangle = (a_H - a_C)\omega_H. \tag{5.84}$$

For this permutation, efficiency is given by the Otto efficiency

$$\eta = \frac{W}{Q} = 1 - \frac{\omega_C}{\omega_H}, \tag{5.85}$$

which is the optimal efficiency.

5.3.3 Thermodynamical framework of self-contained heat engine assisted with a catalyst

This section examines a self-contained heat engine assisted by a catalyst. The engine's state is initialized as

$$\tau^{\mathrm{i}}_{SHCW} = \rho_S \otimes \tau_{\beta_H} \otimes \tau_{\beta_C} \otimes \rho_W, \tag{5.86}$$

where ρ_S is the state of the working body or catalyst, τ_{β_H} and τ_{β_C} are the states of the hot and cold d-level systems given in Eq. (5.44), and ρ_W is the state of the work storage. It is assumed that the state of the work storage ρ_W is diagonal. The combined final state of the engine is denoted by τ^{f}_{SHCW}, and the total bare Hamiltonian of the system is given by

$$H = H_S + H_H + H_C + H_W, \tag{5.87}$$

where H_S is the Hamiltonian of the catalyst, and H_H, H_C, H_W are the Hamiltonians of the hot and cold d level systems and work storage, respectively, as described in section 5.3.2. The system's transformation is described by some unitary that commutes with the total Hamiltonian and generator of translation of the energy of the work storage (see section 4.3 of chapter 4). Hence, employing lemma 33 from chapter 4, the transformation can be characterized equivalently by a unitary that acts on the catalyst, as well as the hot and cold

d-level systems, as shown below:

$$\tau^{\rm f}_{SHC} = V\tau^{\rm i}_{SHC}V^{\dagger}, \tag{5.88}$$

where $\rho_S \otimes \tau^{\rm i}_{SHC} = \tau_{\beta_H} \otimes \tau_{\beta_C}$. Since the marginal state of the catalyst has to be preserved which allows us to write

$$\mathrm{Tr}_{HC}(\tau^{\rm f}_{SHC}) = \mathrm{Tr}_{HC}(V\tau^{\rm i}_{SHC}V^{\dagger}) = \rho_S. \tag{5.89}$$

We want to emphasize that by maintaining the marginal state of the catalyst, there is an opportunity for correlation between the components of the engine. We shall see implicitly later that allowing correlation among the components increase the work production and efficiency of such an engine

Like the earlier scenario described in section 5.3.2, we define the work done by the engine

$$W = \mathrm{Tr}\Big(H_W(\tau^{\rm f}_{SHCW} - \tau^{\rm i}_{SHCW})\Big), \tag{5.90}$$

that reduces to

$$\begin{aligned} W &= \mathrm{Tr}\Big((H_S + H_H + H_C)(\tau^{\rm i}_{SHC} - \tau^{\rm f}_{SHC})\Big) = \mathrm{Tr}\Big((H_S + H_H + H_C)(\tau^{\rm i}_{SHC} - V\tau^{\rm i}_{SHC}V^{\dagger})\Big) \\ &= \mathrm{Tr}\Big(H_S(\tau^{\rm i}_{SHC} - V\tau^{\rm i}_{SHC}V^{\dagger}) + \mathrm{Tr}\Big((H_H + H_C)(\tau^{\rm i}_{SHC} - V\tau^{\rm i}_{SHC}V^{\dagger}) \\ &= \mathrm{Tr}\Big(H_S(\rho_S - V\tau^{\rm i}_{SHC}V^{\dagger}) + \mathrm{Tr}\Big((H_H + H_C)(\rho_S \otimes \tau_{\beta_H} \otimes \tau_{\beta_C} - V(\rho_S \otimes \tau_{\beta_H} \otimes \tau_{\beta_C})V^{\dagger}) \\ &= \mathrm{Tr}\Big((H_H + H_C)(\rho_S \otimes \tau_{\beta_H} \otimes \tau_{\beta_C} - V(\rho_S \otimes \tau_{\beta_H} \otimes \tau_{\beta_C})V^{\dagger}\Big) = Q_H + Q_C, \end{aligned} \tag{5.91}$$

where we use Eq. (5.88) to write the second equality and Eq. (5.89) use the last equality and we denote

$$\begin{aligned} Q_H &= \mathrm{Tr}\Big(H_H(\rho_S \otimes \tau_{\beta_H} \otimes \tau_{\beta_C} - V(\rho_S \otimes \tau_{\beta_H} \otimes \tau_{\beta_C})V^{\dagger}) \\ Q_C &= \mathrm{Tr}\Big(H_C(\rho_S \otimes \tau_{\beta_H} \otimes \tau_{\beta_C} - V(\rho_S \otimes \tau_{\beta_H} \otimes \tau_{\beta_C})V^{\dagger}). \end{aligned} \tag{5.92}$$

Observe the work done by the engine does not depend on the Hamiltonian of the catalyst. Thus one can assume $H_S = 0$ without loss of generality.

Analogous to the previous scenario discussed in subsection 5.3.2, we describe the amount of heat exchanged from the hot heat bath given by

$$\begin{aligned} Q_H &= \mathrm{Tr}\Big(H_H \mathrm{Tr}_{SCW}\Big(\tau^{\rm i}_{\rm SHCW} - \tau^{\rm f}_{\rm SHCW}\Big)\Big) = \mathrm{Tr}\Big(H_H(\tau_{\beta_H} - \mathrm{Tr}_{SC}(\tau^{\rm f}_{SHC}))\Big) \\ &= \mathrm{Tr}\Big(H_H(\rho_S \otimes \tau_{\beta_H} \otimes \tau_{\beta_C} - V(\rho_S \otimes \tau_{\beta_H} \otimes \tau_{\beta_C})V^{\dagger}). \end{aligned} \tag{5.93}$$

Therefore, the efficiency of the engine is given by $\eta = \frac{W}{Q_H}$.

Now we shall describe the second law for the self-contained heat engine assisted with a catalyst.

Lemma 43 (Positivity of work done implies positivity of heat exchange)**.** *For any entropy non-decreasing transformation $\mathcal{U}$ such that $\mathcal{U}(\tau^i_{SHC}) = \tau^f_{SHC}$ where $\tau^i_{SHC} = \rho_S \otimes \tau_{\beta_H} \otimes \tau_{\beta_C}$ the following relation holds:*

$$W > 0 \Rightarrow Q_H > 0. \tag{5.94}$$

Proof. Proof of this lemma can be easily done in a similar way to the proof of lemma 40. Using Eq. (5.91), we have

$$W > 0 \Rightarrow Q_H + Q_C > 0. \tag{5.95}$$

From entropy decreasing property of the transformation $\mathcal{U}$ we have, $S(\tau^f_{SHC}) = S(\tau^i_{SHC}) + \delta$ for some $\delta \geq 0$. Moreover, employing the non-negativity of relative entropy we have the following:

$$D(\tau^{\mathrm{f}}_{SHC} \| \tau^{\mathrm{i}}_{SHC}) \geq 0, \tag{5.96}$$

implies

$$\begin{aligned}
D(\tau^{\mathrm{f}}_{SHC} \| \tau^{\mathrm{i}}_{SHC}) &= -S(\tau^{\mathrm{f}}_{SHC}) - \mathrm{Tr}(\tau^{\mathrm{f}}_{SHC} \log \tau^{\mathrm{i}}_{SHC}) = -S(\tau^{\mathrm{i}}_{SHC}) - \mathrm{Tr}(\tau^{\mathrm{f}}_{SHC} \log \tau^{\mathrm{i}}_{SHC}) - \delta \\
&= \mathrm{Tr}\Big((\tau^{\mathrm{i}}_{SHC} - \tau^{\mathrm{f}}_{SHC}) \log \tau^{\mathrm{i}}_{SHC}\Big) - \delta \\
&= \mathrm{Tr}\Big((\tau^{\mathrm{i}}_{SHC} - \tau^{\mathrm{f}}_{SHC})(-\beta_H H_H - \beta_C H_C)\Big) - \delta \\
&= -(\beta_H Q_H + \beta_C Q_C) - \delta \geq 0. \qquad (5.97)
\end{aligned}$$

From Eq. (5.97) we have $-(\beta_H Q_H + \beta_C Q_C) \geq \delta \geq 0$. Thus we can provide the following bound on Q_C

$$-\frac{\beta_H}{\beta_C} Q_H \geq Q_C. \tag{5.98}$$

From the positivity of work W,

$$\begin{aligned}
Q_H + Q_C > 0 \quad &\Rightarrow \quad Q_H\Big(1 - \frac{\beta_H}{\beta_C}\Big) > 0 \\
&\Rightarrow \quad Q_H > 0, \qquad (5.99)
\end{aligned}$$

since $\beta_C > \beta_H$. This completes the proof. □

Proposition 44. *Consider entropy non-decreasing transformations $\mathcal{U}_1$ and $\mathcal{U}_2$ acting on $\tau^i_{SHC} = \rho_S \otimes \tau_{\beta_H} \otimes \tau_{\beta_C}$ where τ_{β_H} and τ_{β_C} given in Eq. (5.44), with $\mathcal{U}_1(\tau^i_{SHC}) = \tau^1_{SHC}$ and $\mathcal{U}_2(\tau^i_{SHC}) =$*

τ^2_{SHC} *such that*

$$\begin{aligned} W_1 &= Tr\Big((H_H + H_C)(\tau^i_{SHC} - \tau^1_{SHC})\Big) > 0 \\ W_2 &= Tr\Big((H_H + H_C)(\tau^i_{SHC} - \tau^2_{SHC})\Big) < 0 \\ Q_2 &= Tr\Big(H_H Tr_C\Big(\tau^i_{SHC} - \tau^2_{SHC}\Big)\Big) < 0. \end{aligned} \tag{5.100}$$

Proof. Proof can be done easily in a similar manner to proposition 41. ☐

In the next section, we are going to describe the catalytic advantage in the performance of self-contained heat engines.

5.3.3.1 Catalytic advantage in the performance of self-contained heat engine

In this section, we describe how the presence of a catalyst can provide advantages in the performance of the self-contained heat engine. We proceed by reviewing a few results in this direction. In the work of Sparaciari *et. al* [137], authors showed that it is always possible to reduce the average energy of a system that is in a non-thermal passive state via a unitary that acts jointly on the system and a catalyst. We state their results in the following theorem i.e.,

Lemma 45. *[137] Consider a system P in the passive state $\rho_P = \sum_{i=1}^d p_i|E_i\rangle\langle E_i|$ with a Hamiltonian $H_P = \sum_{i=1}^d E_i|E_i\rangle\langle E_i|$ with $E_i < E_{i+1}$ and $p_i \geq p_{i+1}$ for all i with $d > 2$. There exist unitary operation U and a catalyst in the state ρ_S with a trivial Hamiltonian such that*

$$Tr(H_P\rho_P) > Tr\Big(H_P Tr_S\big(U(\rho_P \otimes \rho_S)U^\dagger\big)\Big) \quad with \tag{5.101}$$

$$Tr_P\big(U(\rho_S \otimes \rho_P)U^\dagger\big) = \rho_S. \tag{5.102}$$

Using this lemma we can see straightforwardly that a self-contained engine assisted with a catalyst has strictly greater work production than a self-contained engine without a catalyst. Consider the self-contained heat engine without any catalyst. Let us assume the initial state of hot and cold d level system is $\tau_{\beta_H} \otimes \tau_{\beta_C}$ as given in Eq. (5.44). To extract the maximal amount of work, $\tau_{\beta_H} \otimes \tau_{\beta_C}$ has to transform via a unitary U such that

$$U(\tau_{\beta_H} \otimes \tau_{\beta_C})U^\dagger \quad \text{is passive.} \tag{5.103}$$

Now employing lemma 45, one can further reduce the average energy of the passive state in presence of a catalyst via a unitary operation. This implies the amount of extracted work in

$$\begin{aligned} W^{\max}_{\text{without catalyst}} &= \text{Tr}\big((H_H + H_C)\tau_{\beta_H} \otimes \tau_{\beta_C}\big) - \text{Tr}\Big((H_H + H_C)U(\tau_{\beta_H} \otimes \tau_{\beta_C})U^{\dagger}\Big) \\ &< \text{Tr}\big((H_H + H_C)\rho_S \otimes \tau_{\beta_H} \otimes \tau_{\beta_C}\big) - \text{Tr}\Big((H_H + H_C)\chi_{SHC}\Big) \\ &= W_{\text{with catalyst}}, \end{aligned} \tag{5.104}$$

where χ_{SHC} is the joint state of the catalyst, hot and cold d-level system after the action of unitary transformation mentioned in the lemma 45. Next, we turn our attention to the efficiency of the engine. In what follows, we would like to show the efficiency of a catalyst assisted self-contained heat engine is strictly greater compared to the maximal efficiency that can be attained by a self-contained heat engine without a catalyst. This we prove in the following theorem.

Theorem 46. *Consider a self-contained heat engine having two d-level systems thermalized wrt. to hot and cold bath at temperature β_H and β_C such that $\beta_C > \beta_H$. We denote the initial state of hot and cold level d-level system τ_{β_H} and τ_{β_C} defined in Eq. (5.44). Let us denote the maximal efficiency of a self-contained engine with d-level system τ_{β_H} and τ_{β_C} without a catalyst as $\eta^{max}_{without\ catalyst}$. Then, there always exists a catalyst assisted self-contained engine with efficiency $\eta_{with\ catalyst}$ such that*

$$\eta_{with\ catalyst} > \eta^{max}_{without\ catalyst}. \tag{5.105}$$

Proof. We begin by considering the self contained engine without any catalyst having two d level systems τ_{β_H} and τ_{β_C} as defined in Eq. (5.44). Let us assume that $U_{\max}$ is the unitary that leads to the optimal efficiency for that heat engine such that

$$U_{\max}(\tau_{\beta_H} \otimes \tau_{\beta_C})U^{\dagger}_{\max} = \sigma_{HC}. \tag{5.106}$$

Note that $\text{Tr}_H(\sigma_{HC})$ should be a passive state, otherwise there exist a local unitary that acts on cold d level system that results a greater efficiency. We shall divide the proof in two cases. First, σ_{HC} is correlated state, second, σ_{HC} is product state. We shall proceed by considering σ_{HC} is a correlated state. In order to prove the claim, we employ a results from [159].

Lemma 47. *(Theorem 1 of [159]) There exists a catalyst state ρ_S and a unitary U such that*

$$\chi_{SHC} = U(\rho_S \otimes \sigma_{HC})U^{\dagger}, \tag{5.107}$$

such that

$$\lambda\Big(Tr_{SH}\big(U(\rho_S \otimes \sigma_{HC})U^{\dagger}\big)\Big) \succ \lambda(Tr_H(\sigma_{HC})), \tag{5.108}$$

$$Tr_{SC}\big(U(\rho_S \otimes \sigma_{HC})U^{\dagger}\big) = Tr_C(\sigma_{HC}), \quad and \tag{5.109}$$

$$Tr_{CH}\Big(U(\rho_S \otimes \sigma_{HC})U^{\dagger}\Big) = \rho_S. \tag{5.110}$$

where $\lambda(\cdot)$ is the vector constructed from eigenvalues of the matrix $\cdot$.

From the Eq. (5.108) and using Schur concavity of ordered energy from lemma 48 we can infer that

$$\mathrm{Tr}(H_C \mathrm{Tr}_H(\sigma_{HC})) > \mathrm{Tr}(H_C \mathrm{Tr}_{SH}(\chi_{SHC})). \tag{5.111}$$

This implies that

$$\begin{aligned} W_{\text{without catalyst}} &= \mathrm{Tr}\big((H_H + H_C)(\tau_{\beta_H} \otimes \tau_{\beta_C} - \sigma_{HC}\big) \\ &= \mathrm{Tr}\big(H_H(\tau_{\beta_H} - \mathrm{Tr}_C(\sigma_{HC})\big) + \mathrm{Tr}\big(H_C(\tau_{\beta_C} - \mathrm{Tr}_H(\sigma_{HC})\big) \\ &< \mathrm{Tr}\big(H_H(\tau_{\beta_H} - \mathrm{Tr}_{SC}(\chi_{SHC})\big) + \mathrm{Tr}\big(H_C(\tau_{\beta_C} - \mathrm{Tr}_{HS}(\chi_{SHC})\big) \\ &= W_{\text{with catalyst}}. \end{aligned} \tag{5.112}$$

where the inequality in the third line follows from Eq. (5.109) and Eq. (5.111). On the other hand, the final state of the hot d-level system is the same in both cases of the self-contained engine with or without catalyst as given in Eq. (5.109). That results in an equal amount of heat exchanged in both cases which implies

$$\eta_{\text{without catalyst}} < \eta_{\text{with catalyst}}. \tag{5.113}$$

Next, we consider the scenario where σ_{HC} is a product state. The possible form of the product state that can be taken by σ_{HC} are

$$\sigma_{HC} = V\tau_{\beta_H} V^\dagger \otimes \tilde{V}\tau_{\beta_C}\tilde{V}^\dagger \quad \text{or} \quad \sigma_{HC} = \quad V\tau_{\beta_C} V^\dagger \otimes \tilde{V}\tau_{\beta_H}\tilde{V}^\dagger, \tag{5.114}$$

where V and $\tilde{V}$ is some local unitary that acts on the Hilbert space of τ_{β_H} and τ_{β_C}. Note that the initial combined state of the hot and cold d-level system of the engine is given by $\tau_{\beta_H} \otimes \tau_{\beta_C}$. Therefore, if $\sigma_{HC} = V\tau_{\beta_H} V^\dagger \otimes \tilde{V}\tau_{\beta_C}\tilde{V}^\dagger$ then one can not extract work as average energy of σ_{HC} will be greater than $\tau_{\beta_H} \otimes \tau_{\beta_C}$.

On the other hand if $\sigma_{HC} = \quad V\tau_{\beta_C} V^\dagger \otimes \tilde{V}\tau_{\beta_H}\tilde{V}^\dagger$ then $\mathrm{Tr}_H(\sigma_{HC}) = \tilde{V}\tau_{\beta_H}\tilde{V}^\dagger$. Since the spectrum of $\tau_{\beta_H} \neq \tau_{\beta_C}$ implies $\tilde{V}\tau_{\beta_H}\tilde{V}^\dagger$ is a non-thermal passive state with respect to Hamiltonian H_C. Therefore for $d > 2$, one can apply lemma 45 to reduce the average energy of the cold d level system with the aid of a catalyst. This results in greater work production with the consumption of equal amounts of heat. For $d = 2$ lemma 45 doesn't hold as any qubit passive state is Gibbs with respect to Hamiltonian H_C at some temperature. In the next section, for $d = 2$, we shall design a protocol that performs with strictly greater efficiency for a self-contained heat engine compared to all the self-contained engines without any catalyst. □

We finally conclude this section with the result regarding monotonicity of the ordered

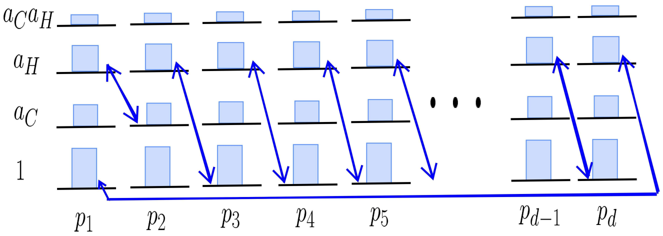

Figure 5.8: **d-level catalyst permutation:** The permutation that leads to $\eta = 1 - \frac{\omega_C}{d\omega_H}$

energy that we have used to prove theorem 46.

Theorem 48 (Schur concavity of ordered energy.)**.** *Consider two diagonal states ρ and σ described by a Hamiltonian $H = \sum_{i=1}^{d} E_i|E_i\rangle\langle E_i|$ with $E_i < E_{i+1}$ for all $i \in 1,\dots,d-1$. If $\lambda(\rho) \succ \lambda(\sigma)$, then the ordered energy of ρ i.e., $Tr(H\rho^{\downarrow}) < Tr(H\sigma^{\downarrow})$ where $\lambda(\cdot)$ is the column vector constructed from the eigenvalues of matrix $\cdot$ and $\rho^{\downarrow}$ (or $\sigma^{\downarrow}$) is the density matrix obtained by rearranging the eigenvalues of ρ (or σ) in non-increasing order.*

Proof. Let us denote the vector constructed from the eigenvalues of H as $\lambda(H)$ i.e.,

$$\lambda(H) = (E_1\ E_2\ \dots\ E_d)^T \quad \text{where} \quad \forall i\ \ E_i < E_{i+1}. \tag{5.115}$$

We can write the following from $\lambda(\rho) \succ \lambda(\sigma)$:

$$\begin{aligned} & \lambda(\rho) \succ \lambda(\sigma) \Rightarrow \lambda(\rho) \succ \lambda^{\downarrow}(\sigma) \Rightarrow B\lambda(\rho) = \lambda^{\downarrow}(\sigma) \Rightarrow \lambda(H)^T B\lambda(\rho) = \lambda(H)^T\lambda^{\downarrow}(\sigma) \\ \Rightarrow\ & \lambda(H)^T\lambda^{\downarrow}(\rho) < \lambda(H)^T B\lambda(\rho) = \lambda(H)^T\lambda^{\downarrow}(\sigma) \\ \Rightarrow\ & \mathrm{Tr}(H\rho^{\downarrow}) < \mathrm{Tr}(H\sigma^{\downarrow}), \end{aligned} \tag{5.116}$$

that completes the proof ☐

5.3.3.2 Smallest self-contained heat engine assisted with a d-level catalyst

Similarly as the smallest autonomous heat engine described in subsection 5.3.2.2, the the hot and cold baths are in equilibrium w.r.t. Hamiltonian $H_H = \omega_H|1\rangle\langle 1|$ and $H_C = \omega_C|1\rangle\langle 1|$ and inverse temperature β_H and β_C. Moreover, we incorporate an auxiliary system or catalyst S represented in the state ρ_S described by a trivial Hamiltonian such that:

$$\rho_S = \sum_{i=1}^{d} p_i|i\rangle\langle i| \tag{5.117}$$

Therefore, the initial joint state of the catalyst, a hot and cold bath is

$$\tau^{\mathrm{i}}_{SHC} = \rho_S \otimes \tau_{\beta_H} \otimes \tau_{\beta_C} \tag{5.118}$$

Therefore,

$$|\tau^{\mathrm{i}}_{SHC}\rangle = \boldsymbol{p} \otimes \frac{1}{1+a_H}(1 \;\; a_H)^T \otimes \frac{1}{1+a_C}(1 \;\; a_C)^T \tag{5.119}$$

where $\boldsymbol{p} = (p_1 \;\; p_2 \;\; \dots \;\; p_d)^T$ and $a_\alpha = e^{-\beta_\alpha \omega_\alpha}$ such that $\alpha \in \{H, C\}$. We shall apply the permutation

$$\Pi_{d-\mathrm{swap}} = S^{d,1}_{3,1} \circ S^{d-1,d}_{3,1} \dots S^{3,4}_{3,1} \circ S^{2,3}_{3,1} \circ S^{1,2}_{3,2} \tag{5.120}$$

where $S^{a,b}_{3,1}$ is a swap between population of level $|a10\rangle_{SHC} \leftrightarrow |b00\rangle_{SHC}$ and $S^{a,b}_{3,2}$ is a swap between population of level $|a10\rangle_{SHC} \leftrightarrow |b01\rangle_{SHC}$ with $a, b \in \{1, \dots, d\}$. In order to put this more simply from Fig. 5.8, $S^{a,b}_{c,d}$ swaps the population between the c^{th} level of a^{th} block and the d^{th} level of b^{th} block where $a, b \in \{1, \dots, d\}$ and $c, d \in \{1, 2, 3, 4\}$.

From the condition of preserving the marginal state of the catalyst, we can write the following:

$$\mathrm{Tr}_{\mathrm{H,\,C}}\big(\Pi_{d-\mathrm{swap}} \tau^{\mathrm{i}}_{SHC} \Pi^{\dagger}_{d-\mathrm{swap}}\big) = \rho_S \tag{5.121}$$

It is straight-forward to see the above-mentioned condition for cyclicity boils down to conserving the population in each block of Fig. 5.8.

$$\text{Block 1:} \qquad p_d a_H - p_1 = p_1 a_H - p_2 a_C \tag{5.122}$$

$$\text{Block 2:} \qquad p_1 a_H - p_2 a_C = p_2 a_H - p_3 \tag{5.123}$$

$$\text{Block 3:} \qquad p_2 a_H - p_3 = p_3 a_H - p_4 \tag{5.124}$$

$$\text{Block 4:} \qquad p_3 a_H - p_4 = p_4 a_H - p_5 \tag{5.125}$$

$$\text{Block 5:} \qquad p_4 a_H - p_5 = p_5 a_H - p_6 \tag{5.126}$$

$$\vdots \qquad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots$$

$$\text{Block k:} \qquad p_{k-1} a_H - p_k = p_k a_H - p_{k+1} \tag{5.127}$$

$$\vdots \qquad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots$$

$$\text{Block d:} \qquad p_{d-1} a_H - p_d = p_d a_H - p_1 \tag{5.128}$$

Thus we can see that

$$\begin{aligned} & p_1 a_H - p_2 a_C = p_2 a_H - p_3 = \dots = p_{d-1} a_H - p_d \\ = \;\; & p_d a_H - p_1 = K \end{aligned} \tag{5.129}$$

Then, the work done by the engine in the swap shown in the Fig. 5.8 can be calculated as

$$\begin{aligned} W &= \langle H|\tau^{\mathrm{i}}_{SHC}\rangle - \langle H|\Pi_{d-\mathrm{swap}}|\tau^{\mathrm{i}}_{SHC}\rangle \\ &= (p_1 a_H - p_2 a_C)(\omega_H - \omega_C) + (p_2 a_H - p_3)\omega_H + \dots \\ &+ (p_{d-1} a_H - p_d)\omega_H + (p_d a_H - p_1)\omega_H \\ &= dK\omega_H - K\omega_C \end{aligned} \tag{5.130}$$

Similarly one can calculate the amount of heat exchanged from the hot reservoir as:

$$\begin{aligned} Q_H &= \langle H_H|\tau^{\mathrm{i}}_{SHC}\rangle - \langle H_H|\Pi_{d-\mathrm{swap}}|\tau^{\mathrm{i}}_{SHC}\rangle \\ &= [(p_1 a_H - p_2 a_C) + (p_2 a_H - p_3) + \dots \qquad (5.131) \\ &+ (p_{d-1} a_H - p_d) + (p_d a_H - p_1)]\omega_H \\ &= dK\omega_H \qquad (5.132) \end{aligned}$$

Thus, To have positive work production W that results from a positive amount of heat exchanged Q_H, we need to have $K > 0$. Adding all the equations from Eq. (5.122) to Eq. (5.128) we have

$$a_H - 1 + p_2 - p_2 a_C = Kd \tag{5.133}$$

$$\Rightarrow \frac{a_H - 1 + p_2 - p_2 a_C}{d} = K \tag{5.134}$$

In order to have $K > 0$, one can see from Eq. (5.133), we need to have $p_2 > \frac{1-a_H}{1-a_C}$. Then, the efficiency can be expressed as

$$\eta = \frac{W}{Q_H} = \frac{Kd\omega_H - K\omega_C}{Kd\omega_H} = 1 - \frac{\omega_C}{d\omega_H} \tag{5.135}$$

From lemma 40, we see that efficiency always have to be less than Carnot bound. Thus

$$\begin{aligned} & 1 - \frac{\omega_C}{d\omega_H} \leq 1 - \frac{\beta_H}{\beta_C} \\ \Rightarrow & \frac{\omega_C}{d\omega_H} \geq \frac{\beta_H}{\beta_C} \quad \Rightarrow \beta_C\omega_C \geq \beta_H\omega_H d \end{aligned} \tag{5.136}$$

Next, we shall explicitly calculate the work production for such a permutation by explicitly calculating p_2 in terms of a_H, and a_C. From Eq. (5.133) we have

$$p_2 = \frac{Kd + 1 - a_H}{1 - a_C}. \tag{5.137}$$

Using this Eq. (5.137) we have

$$\text{For } 3 \leq x \leq d, \quad p_x = a_H^{x-3}\Big(\frac{Kd+1-a_H}{1-a_C}\Big) - K\Big(\frac{1-a_H^{x-2}}{1-a_H}\Big) \tag{5.138}$$

$$\text{and,} \qquad p_1 = \frac{K}{a_H} + \Big(\frac{Kd+1-a_H}{1-a_C}\Big)\frac{a_C}{a_H}. \tag{5.139}$$

Using the normalization of the probability we have,

$$\begin{aligned}
&\sum_{x=3}^{d} p_x = 1 - p_1 - p_2 \\
\Rightarrow\ & \left(\frac{Kd+1-a_H}{1-a_C}\right)\left(\frac{1-a_H^{d-2}}{1-a_H}\right) - \frac{K}{1-a_H}\left(d-2-a_H\Big(\frac{1-a_H^{d-2}}{1-a_H}\Big)\right) = 1 - \left(\frac{Kd+1-a_H}{1-a_C}\right) \\
-\ & \frac{K}{a_H} - \left(\frac{Kd+1-a_H}{1-a_C}\right)\frac{a_C}{a_H} \\
\Rightarrow\ & K = \frac{X}{Y},
\end{aligned} \tag{5.140}$$

where

$$\begin{aligned}
X &= (1-a_H)\left(a_H\left((2-a_C)a_H^2 - (1-a_C)a_C - a_H\right) + (1-a_H)a_H^d\right), \\
Y &= a_H\left(a_C^2(a_H-d+1) + a_C\Big(a_H\big(a_H(d-1)-2\big) + d - 2\Big) + a_H\big(-2a_Hd + a_H + d + 1\big) + 1\right) \\
&+ a_H^d(a_H(a_C+d-1)-d).
\end{aligned} \tag{5.141}$$

Therefore, work production for this engine given by $dK\omega_H - K\omega_C = \frac{X}{Y}(d\omega_H - \omega_C)$. Similarly one can calculate the amount of heat exchanged as $dK\omega_H = d\frac{X}{Y}\omega_H$. In the next section, we are going to explore the dynamical model of the self-contained heat engine with a qubit catalyst.

5.3.3.3 A Dynamical model of a self-contained heat engine with qubit catalyst

A dynamical model of self-contained engine without a catalyst is discussed in [154]. Based on the set-up described in [154], we would like to develop the dynamical model of the self contained heat engine assisted with the catalyst. The heat engine consists of two qubits that are in contact with heat bath at temperature T_H and T_C, a working body. Like the discrete setup, the engine acts by extracting heat from the hot bath and converting it to work. We imagine that the engine produces the work by pulling up a weight. The weight is isolated from both the baths. We assume the weight is raised very slowly such that the change in the potential energy of the weight equalizes amount of extracted work from the engine. Furthermore, we assume that the weight situated at some equidistant heights, such that the difference of energy between two consecutive levels are same. The weight has discrete energy eigenstates $|n\rangle$ with eigenvalue $n\delta$ with $\delta > 0$. Alternatively, we can imagine that the engine delivers work by changing the average energy of an harmonic oscillator. This two cases are almost equivalent, but the energy of harmonic oscillator lower boundeded by zero whereas for the weight there is no lower bound.

We take the Hamiltonian of the qubit H which is in contact with bath of temperature T_H as $H_H = \omega_H |1\rangle\langle 1|$. The state of the qubit τ_H is thermalized at the temperature of the bath, i.e.

$$\tau_H = \frac{1}{1+a_H}\begin{pmatrix} 1 & 0 \\ 0 & a_H \end{pmatrix} \quad \text{where } a_H = e^{-\beta_H \omega_H} \tag{5.142}$$

with $\beta_H = 1/k_B T_H$. The Hamiltonian of the qubit C is given by $H_C = \omega_C |1\rangle\langle 1|$. The state of the qubit τ_C is thermalized at the temperature of the bath, i.e.,

$$\tau_C = \frac{1}{1+a_C}\begin{pmatrix} 1 & 0 \\ 0 & a_C \end{pmatrix} \quad \text{where } a_C = e^{-\beta_C \omega_C} \tag{5.143}$$

with $\beta_C = 1/k_B T_C$. Without loss of generality we take the Hamiltonian of the working body or catalyst (S) as $H_S = 0$. Thus the total free Hamiltonian is given by

$$H_0 = H_H + H_C + H_W^{(1)} + H_W^{(2)} \tag{5.144}$$

where

$$H_W^{(1)} = \sum_{n_1=\infty}^{+\infty} n_1 \mathcal{E} |n_1\rangle\langle n_1| \tag{5.145}$$

$$H_W^{(2)} = \sum_{n_2=-\infty}^{+\infty} n_2 \omega_H |n_2\rangle\langle n_2| \tag{5.146}$$

The energies are taken such that

$$\omega_H - \omega_C = \mathcal{E} \tag{5.147}$$

That implies, the energy levels $|i,1,0,n_1+1,n_2\rangle$ and $|j,0,1,n_1,n_2\rangle$ are degenerate for $i,\ j \in \{1,2\}$. Similarly, the energy levels $|i,1,0,n_1,n_2\rangle$ and $|j,0,0,n_1,n_2+1\rangle$ are degenerate for $i,\ j \in \{1,2\}$. Here we write the vector in the following order $|\cdot\rangle_{SCHW_1W_2}$. The engine operates via doing transitions between these degenerate pair of states.

The qubit and the weight interacts via the Hamiltonian

$$\begin{aligned} H_{\text{int}} = & \sum_{n_1=-\infty}^{+\infty} \sum_{n_2=-\infty}^{+\infty} g\Big(|1,1,0,n_1,n_2\rangle\langle 2,0,1,n_1+1,n_2| \\ + & \ |2,0,1,n_1+1,n_2\rangle\langle 1,1,0,n_1,n_2| \\ + & \ |2,1,0,n_1,n_2\rangle\langle 1,0,0,n_1,n_2+1| \\ + & \ |1,0,0,n_1,n_2+1\rangle\langle 2,1,0,n_1,n_2| \Big) \end{aligned} \tag{5.148}$$

The interaction of the two qubits with their corresponding heat baths is modelled by resetting the qubit in the time interval δt to the corresponding Gibbs state with probability $p_i \delta t$ where $i \in \{H, C\}$. Thus it updates the state in the following manner due to interaction with the bath:

$$p_i \delta t \tau_H \otimes \text{Tr}_i(\rho) + (1 - p_i \delta t)\rho(t) \tag{5.149}$$

The overall equation of motion is

$$\begin{aligned} \frac{d\rho}{dt} &= -i[H_0 + H_{\text{int}}, \rho] + p_H\big(\tau_H \otimes \text{Tr}_H(\rho) - \tau_H\big) \\ &+ \ p_C\big(\tau_C \otimes \text{Tr}_C(\rho) - \tau_C\big) \end{aligned} \tag{5.150}$$

This master equation is consistent in the limit where coupling constant g and dissipation rate with the bath p_H and p_C are small.

We are interested in the change of average energy of the weight

$$\text{Tr}(H_W \rho) = \text{Tr}(H_W^{(1)} \rho) + \text{Tr}(H_W^{(2)} \rho) \tag{5.151}$$

We would like to show that after a transient period, the average energy will increase constantly, that is we expect that

$$\frac{d}{dt}\text{Tr}(H_W \rho) = \text{const} > 0 \tag{5.152}$$

To show that this is the case, we calculate rate of change of average energy of the weight:

$$\frac{d}{dt}\text{Tr}(H_W \rho) = -ig\big(\mathcal{E}\Delta_1(t) + \omega_H \Delta_2(t)\big) \tag{5.153}$$

Here we have

$$\begin{aligned} \Delta_1(t) &= \sum_{n_1,n_2} \big(\langle 1,1,0,n_1,n_2|\rho|2,0,1,n_1+1,n_2\rangle - \langle 2,0,1,n_1+1,n_2|\rho|1,1,0,n_1,n_2\rangle\big) \\ \Delta_2(t) &= \sum_{n_1,n_2} \big(\langle 2,1,0,n_1,n_2|\rho|1,0,0,n_1,n_2+1\rangle - \langle 1,0,0,n_1,n_2+1|\rho|2,1,0,n_1,n_2\rangle\big) \end{aligned} \tag{5.154}$$

To form the complete set of equations we introduce a quantity

$$\Delta_3(t) \;=\; \sum_{n_1,n_2}\big(\langle 2,1,1,n_1,n_2|\rho|1,0,1,n_1,n_2+1\rangle - \langle 1,0,1,n_1,n_2+1|\rho|2,1,1,n_1,n_2\rangle\big) \tag{5.155}$$

Here, we $\Delta_1(t)$, $\Delta_2(t)$ and $\Delta_3(t)$ denote the *translation amplitude* that describes the flow of populations among the desired level.

To form a complete set of equations we have the following:

$$\begin{aligned}
\frac{d\Delta_1(t)}{dt} &= +2ig\big(q_{110}(t)-q_{201}(t)\big)-(p_H+p_C)\Delta_1(t)\\
\frac{d\Delta_2(t)}{dt} &= +2ig\big(q_{210}(t)-q_{100}(t)\big)-(p_H+p_C)\Delta_2(t)+p_Cg_C\big(\Delta_2(t)+\Delta_3(t)\big)\\
\frac{d\Delta_3(t)}{dt} &= p_C(1-g_C)\Delta_2(t)+\big(p_C(1-g_C)-(p_H+p_C)\big)\Delta_3(t)\\
\frac{dq_{100}(t)}{dt} &= -ig\Delta_2(t)-(p_H+p_C)q_{100}(t)+p_Hg_H\big(q_{100}(t)+q_{110}(t)\big)+p_Cg_C\big(q_{100}(t)+q_{101}(t)\big)\\
\frac{dq_{101}(t)}{dt} &= -(p_H+p_C)q_{101}(t)+p_Hg_H\big(q_{101}(t)+q_{111}(t)\big)+p_Cg_C\big(q_{100}(t)+q_{101}(t)\big)\\
\frac{dq_{110}(t)}{dt} &= +ig\Delta_1(t)-(p_H+p_C)q_{110}(t)+p_H(1-g_H)\big(q_{100}(t)+q_{110}(t)\big)+p_Cg_C\big(q_{110}(t)+q_{111}(t)\big)\\
\frac{dq_{111}(t)}{dt} &= -(p_H+p_C)q_{111}(t)+p_H(1-g_H)\big(q_{101}(t)+q_{111}(t)\big)+p_C(1-g_C)\big(q_{110}(t)+q_{111}(t)\big)\\
\frac{dq_{200}(t)}{dt} &= -(p_H+p_C)q_{200}(t)+p_Hg_H\big(q_{200}(t)+q_{210}(t)\big)+p_Cg_C\big(q_{200}(t)+q_{201}(t)\big)\\
\frac{dq_{201}(t)}{dt} &= -ig\Delta_1(t)-(p_H+p_C)q_{201}(t)+p_Hg_H\big(q_{201}(t)+q_{211}(t)\big)+p_C(1-g_C)\big(q_{200}(t)+q_{201}(t)\big)\\
\frac{dq_{210}(t)}{dt} &= +ig\Delta_2(t)-(p_H+p_C)q_{210}(t)+p_H(1-g_H)\big(q_{200}(t)+q_{210}(t)\big)+p_Cg_C\big(q_{210}(t)+q_{211}(t)\big)\\
\frac{dq_{211}(t)}{dt} &= -(p_H+p_C)q_{211}(t)+p_H(1-g_H)\big(q_{201}(t)+q_{211}(t)\big)+p_C(1-g_C)\big(q_{210}(t)+q_{211}(t)\big)
\end{aligned} \tag{5.156}$$

In the matrix form we have the following set of equations:

$$\frac{d\mathbf{v}}{dt} = A\mathbf{v} \tag{5.157}$$

where

$$\mathbf{v} = \Big(\Delta_1(t)\ \Delta_2(t)\ \Delta_3(t)\ q_{100}(t)\ q_{101}(t)\ q_{110}(t)\ q_{111}(t)\ q_{200}(t)\ q_{201}(t)\ q_{210}(t)\ q_{211}(t)\Big)^{\mathrm{T}} \tag{5.158}$$

and

$$A = \begin{bmatrix} \Delta & \text{Int}_1 & \text{Int}_2 \\ \text{Int}_3 & \text{D} & \mathbf{0} \\ \text{Int}_4 & \mathbf{0} & \text{D} \end{bmatrix} \tag{5.159}$$

. Here

$$\Delta = \begin{pmatrix} -(p_H+p_C) & 0 & 0 \\ 0 & p_C g_C - (p_H+p_C) & p_C g_C \\ 0 & p_C(1-g_C) & p_C(1-g_C)-(p_H+p_C) \end{pmatrix} \tag{5.160}$$

$$\text{Int}_1 = \begin{pmatrix} 0 & 0 & +2ig & 0 \\ -2ig & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \quad \text{Int}_2 = \begin{pmatrix} 0 & -2ig & 0 & 0 \\ 0 & 0 & +2ig & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \tag{5.161}$$

$$\text{Int}_3 = \begin{pmatrix} 0 & -ig & 0 \\ 0 & 0 & 0 \\ +ig & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \text{Int}_4 = \begin{pmatrix} 0 & 0 & 0 \\ -ig & 0 & 0 \\ 0 & +ig & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{5.162}$$

and

$$D = \begin{pmatrix} \begin{matrix} p_H g_H + p_C g_C \\ -(p_H+p_C) \end{matrix} & p_C g_C & p_H g_H & 0 \\ p_C(1-g_C) & \begin{matrix} p_H g_H + p_C(1-g_C) \\ -(p_H+p_C) \end{matrix} & 0 & p_H g_H \\ p_H(1-g_H) & 0 & \begin{matrix} p_H(1-g_H) + p_C g_C \\ -(p_H+p_C) \end{matrix} & p_C g_C \\ 0 & p_H(1-g_H) & p_C(1-g_C) & \begin{matrix} p_H(1-g_H) + p_C(1-g_C) \\ -(p_H+p_C) \end{matrix} \end{pmatrix} \tag{5.163}$$

and $\mathbf{0}$ is a block matrix with all the elements equal to 0.

Since we are operating in a weak coupling regime, we expect that the combined state of the engine reaches a non-equilibrium steady state. This implies that when $t \to \infty$ the LHS of equation Eq. (5.157) goes to zero i.e.,

$$0 = A\mathbf{v} \tag{5.164}$$

As a consequence, the transition amplitude $\Delta_1(t)$, $\Delta_2(t)$ and $\Delta_3(t)$ become constant in the limit $t \to \infty$ i.e.,

$$\lim_{t\to\infty} \Delta_1(t) = C_1 \quad ; \quad \lim_{t\to\infty} \Delta_2(t) = C_2 \quad ; \quad \lim_{t\to\infty} \Delta_3(t) = C_3. \tag{5.165}$$

The quantity of interest that is the rate of the average energy of the work storage considered in Eq. (5.153) in the limit $t \to \infty$:

$$\begin{aligned} \lim_{t\to\infty} \frac{d}{dt}\mathrm{Tr}(H_W \rho) &= -ig\big(\mathcal{E} \lim_{t\to\infty} \Delta_1(t) + \omega_H \lim_{t\to\infty} \Delta_2(t)\big) = -ig(\mathcal{E}C_1 + \omega_H C_2) \\ &= -ig((C_1 + C_2)\omega_H - C_2\omega_C), \end{aligned} \tag{5.166}$$

where we put $\mathcal{E} = \omega_H - \omega_C$. This implies after a transient period, the average energy will increase uniformly. In a similar manner, we can define the rate of change of heat for the master equation in Eq. (5.150) as

$$\frac{dQ_H}{dt} := p_H \mathrm{Tr}\big(H_H(\tau_{\beta_H} - \rho_H(t))\big), \tag{5.167}$$

where $\rho_H(t)$ is the state of the hot d level system at time t. In the steady state we have $\lim_{t\to\infty} \rho_H(t) = \rho_H$ then we can reduce the expression given in Eq. (5.167)

$$\lim_{t\to\infty} \frac{dQ_H}{dt} = \lim_{t\to\infty} p_H \mathrm{Tr}\big(H_H(\tau_{\beta_H} - \rho_H(t))\big) = \mathrm{Tr}\big(H_H(\tau_{\beta_H} - \rho_H)\big) = p_H\omega_H\big((1-g_H) - K_1\big), \tag{5.168}$$

where $K_1 = \lim_{t\to\infty} q_{110}(t) + q_{111}(t) + q_{210}(t) + q_{211}(t)$. Employing Eq. (5.156) we can write the following:

$$\begin{aligned} 0 = \frac{dK_1}{dt} &= \lim_{t\to\infty} \frac{d}{dt}\big(q_{110}(t) + q_{111}(t) + q_{210}(t) + q_{211}(t)\big) \\ &= \lim_{t\to\infty} \Big(+ ig\big(\Delta_1(t) + \Delta_2(t)\big) + p_H(1-g_H) - p_H\big(q_{110}(t) + q_{111}(t) + q_{210}(t) + q_{211}(t)\big)\Big) \\ &= +ig(C_1 + C_2) + p_H(1-g_H) - p_H K_1. \end{aligned} \tag{5.169}$$

Using the obtained expression in Eq. (5.169), we can write

$$\lim_{t\to\infty} \frac{dQ_H}{dt} = (1-g_H)p_H\omega_H - p_H\omega_H K_1 = -ig\omega_H(C_1 + C_2). \tag{5.170}$$

In the limit $t \to \infty$ the marginal state of the catalyst also reaches the steady state i.e.,

$$\lim_{t\to\infty} \rho_S(t) = \mathrm{Tr}_{HC}\rho(t) = \rho_0. \tag{5.171}$$

This implies

$$\begin{aligned} 0 &= \lim_{t\to\infty} \frac{d}{dt}\rho_S(t) = 0 \Rightarrow \lim_{t\to\infty} \frac{d}{dt}\big(q_{100}(t) + q_{101}(t) + q_{110}(t) + q_{111}(t)\big) = \lim_{t\to\infty} -ig(\Delta_2(t) - \Delta_1(t)) \\ &= -ig(C_2 - C_1) \Rightarrow C_1 = C_2. \end{aligned} \tag{5.172}$$

Therefore, the efficiency can be expressed as

$$\eta = \frac{\lim_{t\to\infty}\frac{dW}{dt}}{\lim_{t\to\infty}\frac{dQ_H}{dt}} = \frac{-ig\omega_H(C_1+C_2)+igC_2\omega_C}{-ig\omega_H(C_1+C_2)} = 1-\frac{C_2}{C_1+C_2}\frac{\omega_C}{\omega_H} = 1-\frac{\omega_C}{2\omega_H}, \tag{5.173}$$

where we use $C_1 = C_2$ to write the last equality. On the other hand, in order to explicitly calculate the rate of change of average energy stored in the work storage (also referred as *power*) from Eq. (5.166), we need to calculate the constants C_1 and C_2. By solving the equation for steady state from Eq. (5.164), we obtain

$$C_1 = C_2 = ig\frac{a}{b} \tag{5.174}$$

where

$$\begin{align} a &= 2g_Cp_Cp_H\Big(2g_C(g_H-1)g_H+g_C-g_H^2\Big)(p_C+p_H)(g_Cp_C+p_H) \nonumber\\ b &= p_Cp_H(p_C+p_H)^2\Big(g_C^2p_C-2g_C(g_H-1)p_H+g_Hp_H\Big) \tag{5.175}\\ &- 2g^2(g_Cp_C+p_H)\Big(-p_H^2\Big(2g_C(g_H-1)g_H+g_C-g_H^2+g_H\Big) \nonumber\\ &+ g_Cp_C^2(g_C(4g_H-2)-2g_H-1)+2p_Cp_H(2g_C(g_H-1)-g_H)\Big) \tag{5.176} \end{align}$$

Therefore the power of the engine is given by

$$\lim_{t\to\infty}\frac{d}{dt}\mathrm{Tr}(H_W\rho) = -ig((C_1+C_2)\omega_H - C_2\omega_C) = g^2\frac{a}{b}(2\omega_H-\omega_C). \tag{5.177}$$

This analysis can be extended to a scenario of d level catalyst easily where one can obtain efficiency $\eta = 1-\frac{\omega_C}{d\omega_H}$. But the calculation of power in that scenario is not very straightforward as it requires solving a higher number of equations to reach the steady state solutions.

5.4 Conclusions and outlook

In this chapter, we utilized the concept of ergotropy extraction to develop an open-cycle engine within the realm of quantum mechanics. The engine is designed to operate during strokes, and we demonstrated that maximum efficiency and work output can be achieved by utilizing extreme states of the thermal polytope of the initial state. Analytical means were used to identify optimal protocols for work production and efficiency in engines operating in two and three dimensions, while higher dimensional scenarios were analyzed numerically.

We then introduced the self-contained engine in the microscopic regime, which transforms via a global unitary to conserve the total energy of the engine. We established a thermodynamic framework to assess the optimal performance of the heat engine and analytically calculated its optimal efficiency. Additionally, we showed how the performance of a self-contained engine can be enhanced by a catalyst through a constructed protocol, and provided a dynamical model that simulates the catalytic advantages in the microscopic heat engine.

There are several interesting open problems that could be further investigated. For instance, we numerically observed that the efficiency of a self-contained engine aided with a d-dimensional catalyst is optimal when $\eta = 1 - \frac{\omega_C}{d\omega_H}$, and it would be interesting to analytically prove this. We also simulated a self-contained engine aided with a two-level catalyst via a dynamical model, but this analysis could be extended for arbitrary d-dimensional catalysts to calculate the power output from the engine. Finally, investigating the time scale at which the dynamical model produces the same work as that given by self-contained engines would also be an interesting avenue to explore.

Chapter 6

Appendix

6.1 Proof of Birkhoff von Neumann theorem

In this appendix, we shall provide the proof for the Birkhoff von Neumann theorem.

Theorem 49 (Birkhoff's theorem)**.** *The set of all Bistochastic matrices is convex and The extremal point of this set are given by permutation matrices. In other words any bistochastic matrices can be written as convex sum of of permutation matrices i.e.,*

$$T = \sum_{i}^{d!} \lambda_i \Pi_i \tag{6.1}$$

where $\forall i \quad \lambda_i \geq 0$ *and* $\sum_{i=1}^{d!} \lambda_i = 1$.

Proof. It is very straightforward to see that set of all bistochastic matrices forms a convex set. Taking the convex sum of two bistochastic matrices B_1 and B_2 one can easily check that as follows:

$$\begin{aligned} \sum_{i=1}^{d} \Big(\lambda (B_1)_{ij} + (1-\lambda)(B_2)_{ij} \Big) = \lambda \sum_{i=1}^{d} (B_1)_{ij} + (1-\lambda) \sum_{i=1}^{d} (B_2)_{ij} &= 1 \\ \sum_{j=1}^{d} \Big(\lambda (B_1)_{ij} + (1-\lambda)(B_2)_{ij} \Big) = \lambda \sum_{j=1}^{d} (B_1)_{ij} + (1-\lambda) \sum_{i=1}^{d} (B_2)_{ij} &= 1 \end{aligned} \tag{6.2}$$

We would like to show the extremal points of the set of permutation matrices given by permutation matrices. We shall prove the claim by contradiction. Let us assume that A is an extremal point of the set of bistochastic matrices that is not a permutation. Then there is at least one row of A, say row i_1 that contains two non-zero entries. Choosing one non-zero entry from row i_1 which we shall denote by $A_{i_1 i_2}$. Since there are two non-zero entries in the row i_1 we shall have $0 < A_{i_1 i_2} < 1$.

From the bistochastisity of the matrix A and employing $0 < A_{i_1 i_2} < 1$, we can conclude that there exist at least one element $A_{i_3 i_2}$ in the column i_2 such that $0 < A_{i_3 i_2} < 1$ where $i_3 \neq i_1$. Since $0 < A_{i_3 i_2} < 1$, there is at least one element $A_{i_3 i_4}$ in the row i_3 such that $0 < A_{i_3 i_4} < 1$.

If this process is continued and the successive entries are chosen in this way are marked, after finitely many steps there will be the first time that an element A_{ij} is chosen that has previously been chosen. The sequence of elements from the first up to the second occurrence of the entry A_{ij} is finite such that each successive entries are in different columns or rows. We call this sequence J.

Let ϵ be the smallest entry in the sequence J. Let C be a matrix in which $+1$ appears in the location of the first element of the sequence J and -1 appears in the location of the second element on that sequence J. Then $+1$ appears on the location of the third element of the sequence and -1 appears on the location of the fourth element of the sequence and so on. Define

$$A_+ = A + \epsilon C \quad ; \quad A_- = A - \epsilon C \tag{6.3}$$

Note that all the entries of A_+ and A_- are non-negative since ϵ is the smallest entry in the sequence J. Thus A_+ and A_- are bistochastic matrix. Then A is

$$A = \frac{1}{2} A_+ + \frac{1}{2} A_- \tag{6.4}$$

Therefore, A is not an extremal point of the set of bistochastic matrices. □

6.2 Optimality of the communication rate

This derivation closely follows the proof of Lemma 1 of [115]. Consider a system (ρ^N, H^N), where M number of messages can be encoded in a thermodynamically-free manner, such that the error associated with average decoding is ϵ. This implies that there exists a set of M encoding thermal operations $\{\mathcal{E}_i\}_{i=1}^M$ and a decoding POVM $\Pi_i i = 1^M$ such that the following equality holds:

$$1 - \epsilon = \frac{1}{M} \sum_{i=1}^{M} \mathrm{Tr}\left(\mathcal{E}_i(\rho^N) \Pi_i\right). \tag{6.5}$$

Note that, the thermal equilibrium state is invariant under any thermal operation $\mathcal{E}_i$ that transforms the initial system (ρ^N, H^N) and a target system $(\tilde{\rho}^N, \tilde{H}^N)$ i.e.,

$$\mathcal{E}_i(\gamma^N) = \tilde{\gamma}^N. \tag{6.6}$$

Now, let us introduce three states in the following manner

$$\tau :=\frac{1}{M}\sum_{i=1}^{M}|i\rangle\langle i|\otimes\mathcal{E}_i(\rho^N), \tag{6.7a}$$

$$\zeta :=\frac{1}{M}\sum_{i=1}^{M}|i\rangle\langle i|\otimes\gamma^N, \tag{6.7b}$$

$$\tilde{\zeta} :=\frac{1}{M}\sum_{i=1}^{M}|i\rangle\langle i|\otimes\tilde{\gamma}^N. \tag{6.7c}$$

The hypothesis testing relative entropy D_H^ϵ between τ and $\tilde{\zeta}$, given by [160, 161, 162]

$$\begin{aligned}D_H^\epsilon(\tau\|\tilde{\zeta}):= -\log\inf\Big\{\mathrm{Tr}\left(Q\tilde{\zeta}\right)\ \Big|\ 0\le Q\le\mathbb{1},&\\ \mathrm{Tr}\left(Q\tau\right)\ge 1-\epsilon\Big\},&\end{aligned} \tag{6.8}$$

that satisfies the following relation

$$D_H^\epsilon(\tau\|\tilde{\zeta}) \ge -\log\mathrm{Tr}\left(Q\tilde{\zeta}\right) \tag{6.9}$$

for

$$Q=\sum_{i=1}^{M}|i\rangle\langle i|\otimes\Pi_i. \tag{6.10}$$

This is because the above (potentially suboptimal) choice of Q given in Eq. (6.10) clearly satisfies $0\le Q\le\mathbb{1}$ and also

$$\mathrm{Tr}\left(Q\tau\right)=\frac{1}{M}\sum_{i=1}^{M}\mathrm{Tr}\left(\mathcal{E}_i(\rho)\Pi_i\right)\ge 1-\epsilon, \tag{6.11}$$

due to our assumption in Eq. (6.5). Simultaneously, we have

$$\mathrm{Tr}\left(Q\tilde{\zeta}\right)=\frac{1}{M}\sum_{i=1}^{M}\mathrm{Tr}\left(\tilde{\rho}^N\Pi_i\right)=\frac{1}{M}, \tag{6.12}$$

so that

$$\log M\le D_H^\epsilon(\tau\|\tilde{\zeta}). \tag{6.13}$$

Next, we define the following encoding channel

$$\mathcal{F}:=\sum_{i=1}^{M}|i\rangle\langle i|\otimes\mathcal{E}_i, \tag{6.14}$$

that satisfies

$$\mathcal{F}(\zeta) = \tilde{\zeta}. \tag{6.15}$$

Using the data-processing inequality twice, we get the sequence of inequalities as follows:

$$\begin{aligned} D_H^\epsilon(\tau\|\tilde{\zeta}) &= D_H^\epsilon\left(\mathcal{F}\left(\frac{1}{M}\sum_{i=1}^{M}|i\rangle\langle i|\otimes\rho^N\right)\middle\|\mathcal{F}(\zeta)\right) \\ &\leq D_H^\epsilon\left(\frac{1}{M}\sum_{i=1}^{M}|i\rangle\langle i|\otimes\rho^N\middle\|\zeta\right) \\ &\leq D_H^\epsilon(\rho^N\|\gamma^N). \end{aligned} \tag{6.16}$$

Combining this with Eq. (6.13), we arrive at

$$\log M \leq D_H^\epsilon(\rho^N\|\gamma^N). \tag{6.17}$$

Finally, for the case of identical initial subsystems, $\rho^N = \rho^{\otimes N}$ and $\gamma^N = \gamma^{\otimes N}$, one can use the known second order asymptotic expansion of the hypothesis testing relative entropy [163],

$$\frac{1}{N}D_H^\epsilon(\rho^{\otimes N}\|\gamma^{\otimes N}) \simeq D(\rho\|\gamma) + \sqrt{\frac{V(\rho\|\gamma)}{N}}\Phi^{-1}(\epsilon), \tag{6.18}$$

that leads to

$$\frac{\log M}{N} \lesssim D(\rho\|\gamma) + \sqrt{\frac{V(\rho\|\gamma)}{N}}\Phi^{-1}(\epsilon). \tag{6.19}$$

For the above proof to work also in the case of non-identical subsystems, where one would need to prove the following asymptotic behaviour of the hypothesis testing relative entropy:

$$\begin{aligned} &\frac{1}{N}D_H^\epsilon\left(\bigotimes_{n=1}^{N}\rho_n\middle\|\bigotimes_{n=1}^{N}\gamma_n\right) \\ &\simeq \frac{1}{N}\sum_{n=1}^{N}D(\rho_n\|\gamma_n) + \sqrt{\frac{\frac{1}{N}\sum\limits_{n=1}^{N}V(\rho_n\|\gamma_n)}{N}}\Phi^{-1}(\epsilon). \end{aligned} \tag{6.20}$$

6.3 Proof of lemma 31

Proof. Let us assume $\tilde{\boldsymbol{q}}$ to be a classical state that saturates $\boldsymbol{p} \succ_\epsilon \boldsymbol{q}$. By definition it implies that $\boldsymbol{p} \succ \tilde{\boldsymbol{q}}$ and $F(\boldsymbol{q}, \tilde{\boldsymbol{q}}) = 1 - \epsilon$. As $V(\boldsymbol{q}) = 0$ and $H(\boldsymbol{q}) = \log L$, the classical state $\boldsymbol{q}$ contains exactly L non-zero entries such that each of them is equal to $1/L$. Thus,

$$\boldsymbol{q}^{\downarrow} = \Big(\underbrace{\frac{1}{L}, \dots, \frac{1}{L}}_{L}, 0, \dots, 0\Big). \tag{6.21}$$

From the definition of $F(\boldsymbol{q}, \tilde{\boldsymbol{q}})$ given in Eq. (3.51) we can write the following

$$\begin{aligned} 1 - \epsilon = F(\boldsymbol{q}, \tilde{\boldsymbol{q}}) &\leq F(\boldsymbol{q}^{\downarrow}, \tilde{\boldsymbol{q}}^{\downarrow}) \\ &= \frac{1}{L}\left(\sum_{i=1}^{L} \sqrt{\tilde{q}_i^{\downarrow}}\right)^2 = \frac{1}{L}\left(\sum_{i=1}^{L} \sqrt{\tilde{q}_i^{\downarrow} \cdot 1}\right)^2 \\ &\leq \frac{1}{L}\left(\sum_{i=1}^{L} \tilde{q}_i^{\downarrow}\right)\left(\sum_{i=1}^{L} 1\right) = \sum_{i=1}^{L} \tilde{q}_i^{\downarrow}, \end{aligned} \tag{6.22}$$

where the first inequality follows from the definition of fidelity, while the second one comes from the Cauchy-Schwarz inequality. Now, from lemma 31, we have

$$\sum_{i=1}^{L} p_i^{\downarrow} = 1 - \epsilon. \tag{6.23}$$

Combining this with Eq. (6.22) we obtain

$$\sum_{i=1}^{L} p_i^{\downarrow} \leq \sum_{i=1}^{L} \tilde{q}_i^{\downarrow}. \tag{6.24}$$

On the other hand, $\boldsymbol{p} \succ \tilde{\boldsymbol{q}}$ gives

$$\sum_{i=1}^{L} p_i^{\downarrow} \geq \sum_{i=1}^{L} \tilde{q}_i^{\downarrow}, \tag{6.25}$$

and thus we conclude that

$$\sum_{i=1}^{L} p_i^{\downarrow} = \sum_{i=1}^{L} \tilde{q}_i^{\downarrow} = 1 - \epsilon. \tag{6.26}$$

Next, note that as $\epsilon = 1 - F(\boldsymbol{q}, \tilde{\boldsymbol{q}}) \geq 1 - F(\boldsymbol{q}^{\downarrow}, \tilde{\boldsymbol{q}}^{\downarrow})$, we see that to have the minimal value of error, $\tilde{\boldsymbol{q}}^{\downarrow}$ needs to maximize the fidelity $F(\boldsymbol{q}^{\downarrow}, \tilde{\boldsymbol{q}}^{\downarrow})$ subjected to the constraint given in Eq. (6.26). Thus we can write

$$\begin{aligned} &\max && \frac{1}{L}\left(\sum_{i=1}^{L}\sqrt{\tilde{q}_i^{\downarrow}}\right)^2 \\ &\text{such that} && \sum_{i=1}^{L}\tilde{q}_i^{\downarrow} = 1-\epsilon. \end{aligned} \tag{6.27}$$

The Lagrangian of the above optimization problem given in Eq. (6.27) can be expressed as

$$\mathcal{L} = \frac{1}{L}\left(\sum_{i=1}^{L}\sqrt{\tilde{q}_i^{\downarrow}}\right)^2 - \lambda\left(\sum_{i=1}^{L}\tilde{q}_i^{\downarrow} - 1 + \epsilon\right), \tag{6.28}$$

where λ is a Lagrange multiplier. To find the solution to the problem we calculate

$$\frac{\partial\mathcal{L}}{\partial\tilde{q}_j^{\downarrow}} = \frac{1}{\left(L\sqrt{\tilde{q}_j^{\downarrow}}\right)}\left(\sum_{i=1}^{L}\sqrt{\tilde{q}_i^{\downarrow}}\right) - \lambda \tag{6.29}$$

for all $j \in \{1,\ldots,L\}$. By solving $\partial\mathcal{L}/\partial\tilde{q}_j^{\downarrow} = 0$ we obtain

$$\tilde{q}_j^{\downarrow} = \left(\frac{1}{\lambda L}\left(\sum_{i=1}^{L}\sqrt{\tilde{q}_i^{\downarrow}}\right)\right)^2 \tag{6.30}$$

for all $j \in \{1,\ldots,L\}$. Substituting $\tilde{q}_j^{\downarrow}$ from Eq. (6.30) to the constraint specified in Eq. (6.26) gives

$$\lambda = \frac{1}{\sqrt{(1-\epsilon)L}}\left(\sum_{i=1}^{L}\sqrt{\tilde{q}_i^{\downarrow}}\right). \tag{6.31}$$

Thus, substituting λ from Eq. (6.31) into Eq. (6.30) finally gives

$$\forall i \in \{1,\ldots,L\}: \qquad \tilde{q}_i^{\downarrow} = \frac{1-\epsilon}{L}. \tag{6.32}$$

Since fidelity is a concave function, and the constraint defined in Eq. (6.27) is linear, this solution is optimal.

Next, we note that $\boldsymbol{p} \succ \tilde{\boldsymbol{q}}$ implies $Q\boldsymbol{p}^{\downarrow} = \tilde{\boldsymbol{q}}^{\downarrow}$ where Q is a bistochastic matrix. Since any Q can be decomposed as a convex sum of permutations (see theorem 6.1), we can write

$$Q = \sum_i \alpha_i \Pi_i, \tag{6.33}$$

where Π_i is a permutation matrix and $\sum_i \alpha_i = 1$ with $\alpha_i \in [0,1]$ for all i. Let us introduce a vector $\boldsymbol{v}$ as

$$\boldsymbol{v} := \Big(\underbrace{1,\ldots,1}_{L},0\ldots,0\Big). \tag{6.34}$$

Using this $\boldsymbol{v}$, we can write the following

$$\begin{aligned} &\boldsymbol{v}\cdot Q\boldsymbol{p}^{\downarrow} = \boldsymbol{v}\cdot\tilde{\boldsymbol{q}}^{\downarrow} = \boldsymbol{v}\cdot\boldsymbol{p}^{\downarrow} = (1-\epsilon) \\ \Rightarrow\quad &\sum_i \alpha_i \boldsymbol{v}\cdot\Pi_i\boldsymbol{p}^{\downarrow} = \boldsymbol{v}\cdot\boldsymbol{p}^{\downarrow} \end{aligned} \tag{6.35}$$

where we use Eq. (6.26) in the first line, and the convex decomposition of Q from Eq. (6.33) in the second line. Note that Eq. (6.35) can be equivalently written as

$$\sum_i \alpha_i(\Pi_i^T\boldsymbol{v})\cdot\boldsymbol{p}^{\downarrow} = \boldsymbol{v}\cdot\boldsymbol{p}^{\downarrow}, \tag{6.36}$$

where Π_i^T is the transpose of the permutation matrix Π_i. Since the elements of $\boldsymbol{v}$ and $\boldsymbol{p}^{\downarrow}$ are arranged in the decreasing order, the maximum value of $(\Pi_i^T\boldsymbol{v})\cdot\boldsymbol{p}^{\downarrow}$ is $\boldsymbol{v}\cdot\boldsymbol{p}^{\downarrow}$. Thus, we see that equality in Eq. (6.36) holds if and only if $\boldsymbol{v}$ is invariant under (Π_i^T) for all i. Therefore, Π_i can be only of the form

$$\Pi_i = \Pi_i^L \oplus \Pi_i^{L^c}, \tag{6.37}$$

where Π_i^L and $\Pi_i^{L^c}$ are the permutations that act trivially for indices $i > L$ and $i \in \{1,\ldots,L\}$, respectively. Thus, we conclude using Eq. (6.33) that Q is a block-diagonal matrix of the form

$$Q = \tilde{B}\oplus B, \tag{6.38}$$

where $\tilde{B}$ and B are $L\times L$ and $(d-L)\times(d-L)$ bistochastic matrices. Hence,

$$\forall i > L,\quad \tilde{q}_i^{\downarrow} = \sum_{j>L} B_{ij}p_j^{\downarrow}. \tag{6.39}$$

Combining Eq. (6.32) and Eq. (6.39) we conclude that $\tilde{\boldsymbol{q}}^{\downarrow} = \boldsymbol{q}^{*\downarrow}$ with $\boldsymbol{q}^*$ defined in Eq. (3.98). This finally implies $\tilde{\boldsymbol{q}} = \Pi\boldsymbol{q}^*$ with Π being some permutation. Finally, it is easy to conclude that the minimal entropy of $\boldsymbol{q}^*$ is achieved for B being the identity matrix, since the entropy is always increasing under the application of any non-trivial bistochastic matrix. □

6.4 Eliminating the logarithmic term

We start with the following lemma that will be required to prove our claim.

Lemma 50. *For a fixed value of $b > 0$ and any $\boldsymbol{s}$, such that $\|\boldsymbol{s}\| = \sqrt{\sum_{i=1}^{d} s_i^2} \leq b$, we have*

$$\log P^N_{\boldsymbol{k}(\boldsymbol{s})} = O(\log N), \tag{6.40}$$

where $P^N_{\boldsymbol{k}}$ and $\boldsymbol{k}(\boldsymbol{s})$ are defined by Eq. (3.131) and Eq. (3.139), respectively.

Proof. We start by using the definition,

$$P^N_{\boldsymbol{k}(\boldsymbol{s})} = \binom{N}{k_1(s_1), ..., k_d(s_d)} p_1^{k_1(s_1)} ... p_d^{k_d(s_d)}, \tag{6.41}$$

to write $\log P^N_{\boldsymbol{k}(\boldsymbol{s})}$ as

$$\log P^N_{\boldsymbol{k}(\boldsymbol{s})} = \log N! - \sum_{i=1}^{d} \log k_i(s_i)! + \sum_{i=1}^{d} k_i(s_i) \log p_i. \tag{6.42}$$

Using the Stirling inequality,

$$\begin{aligned} &\log \sqrt{N} + N \log N - N \\ &\quad \leq \log N! \leq \\ &\qquad 1 + \log \sqrt{N} + N \log N - N, \end{aligned} \tag{6.43}$$

we first give a lower bound for $\log P^N_{\boldsymbol{k}(\boldsymbol{s})}$ as follows:

$$\begin{aligned} \log P^N_{\boldsymbol{k}(\boldsymbol{s})} \geq & (\log \sqrt{N} + N \log N - N) + \sum_{i=1}^{d} k_i(s_i) \log p_i \\ & - \sum_{i=1}^{d} (1 + \log \sqrt{k_i(s_i)} + k_i(s_i) \log k_i(s_i) - k_i(s_i)) \\ = & - \sum_{i=1}^{d} k_i(s_i) \log \left(\frac{k_i(s_i)}{N p_i} \right) - d \\ & + \frac{1}{2} \Big(\log N - \sum_{i=1}^{d} \log k_i(s_i) \Big). \end{aligned} \tag{6.44}$$

Recall that $k_i(s_i) = N p_i + \sqrt{N} s_i$, that implies $\sum_{i=1}^{d} s_i = 0$. In order to simplify the above further, we lower bound the first term by employing the inequality $\log(1 + g) < g$ for $g >$

-1 in the following manner:

$$\begin{aligned}\sum_{i=1}^{d} k_i(s_i)\log\left(\frac{k_i(s_i)}{Np_i}\right) &= \sum_{i=1}^{d} k_i(s_i)\log\left(1+\frac{s_i}{\sqrt{N}p_i}\right)\\ &\leq \sum_{i=1}^{d} k_i(s_i)\frac{s_i}{\sqrt{N}p_i} = \sqrt{N}\sum_{i=1}^{d}(1+\frac{s_i}{\sqrt{N}p_i})s_i\\ &= \sum_{i=1}^{d}\frac{s_i^2}{p_i} \leq \sum_{i=1}^{d}\frac{s_i^2}{p_{\min}} \leq \frac{b^2}{p_{\min}},\end{aligned} \tag{6.45}$$

where $p_{\min} = \min\{p_1, \ldots, p_d\}$. Moreover, noting that

$$\log N \geq \left(\log N - \sum_{i=1}^{d}\log k_i(s_i)\right) \geq -(d-1)\log N, \tag{6.46}$$

we can conclude

$$\log N - \sum_{i=1}^{d}\log k_i(s_i) = O(\log N). \tag{6.47}$$

Putting it together, one further simplify the bound given in Eq. (6.44) as

$$\log P^N_{\boldsymbol{k}(\boldsymbol{s})} \geq -d - \frac{b^2}{p_{\min}} - \frac{(d-1)}{2}\log N = O(\log N). \tag{6.48}$$

Similarly, by employing the Stirling inequality from Eq. (6.43), one can also prove an upper bound for $\log P^N_{\boldsymbol{k}(\boldsymbol{s})}$ as follows

$$\begin{aligned}\log P^N_{\boldsymbol{k}(\boldsymbol{s})} \leq& (1+\log\sqrt{N}+N\log N - N) + \sum_{i=1}^{d} k_i(s_i)\log p_i\\ &- \sum_{i=1}^{d}\left(\log\sqrt{k_i(s_i)} + k_i(s_i)\log k_i(s_i) - k_i(s_i)\right)\\ =& -\sum_{i=1}^{d} k_i(s_i)\log\left(\frac{k_i(s_i)}{Np_i}\right) + 1\\ &+ \frac{1}{2}(\log N - \sum_{i=1}^{d}\log k_i(s_i)).\end{aligned} \tag{6.49}$$

Employing the inequality $\log(1+g) \geq \frac{g}{1+g}$ for $g > -1$, we have

$$\begin{aligned}\sum_{i=1}^{d} k_i(s_i) \log\left(\frac{k_i(s_i)}{Np_i}\right) &= \sum_{i=1}^{d} k_i(s_i) \log\left(1 + \frac{s_i}{\sqrt{N}p_i}\right) \\ &\geq \sum_{i=1}^{d} k_i(s_i) \frac{s_i}{s_i + \sqrt{N}p_i} = \sqrt{N} \sum_{i=1}^{d} s_i = 0. \end{aligned} \tag{6.50}$$

The above inequality together with Eq. (6.47) imply that $\log P^N_{\boldsymbol{k}(\boldsymbol{s})} \leq O(\log N)$ that completes the proof.

□

Using lemma 50, we will now be able to prove our claim that is captured by the following result.

Lemma 51. *The following limits are equal:*

$$\begin{aligned}&\lim_{N\to\infty} \sum_{\boldsymbol{s}} \Big\{ P^N_{\boldsymbol{k}(\boldsymbol{s})} \Big| \frac{1}{N} \log(P^N_{\boldsymbol{k}(\boldsymbol{s})}) + \frac{\beta}{\sqrt{N}} \sum_i s_i E_i \\ &\qquad + F^N_{\text{diss}} \geq 0 \Big\} \\ &= \lim_{N\to\infty} \sum_{\boldsymbol{s}} \Big\{ P^N_{\boldsymbol{k}(\boldsymbol{s})} \Big| \frac{\beta}{\sqrt{N}} \sum_i s_i E_i + F^N_{\text{diss}} \geq 0 \Big\}. \end{aligned} \tag{6.51}$$

Proof. We start by introducing the following notation

$$\begin{aligned} A(N) &:= \sum_{\boldsymbol{s}} \Big\{ P^N_{\boldsymbol{k}(\boldsymbol{s})} \Big| \frac{1}{N} \log(P^N_{\boldsymbol{k}(\boldsymbol{s})}) + \frac{\beta}{\sqrt{N}} \sum_i s_i E_i \\ &\qquad + F^N_{\text{diss}} \geq 0 \Big\}, \\ A(b,N) &:= \sum_{\boldsymbol{s}} \Big\{ P^N_{\boldsymbol{k}(\boldsymbol{s})} \Big| \frac{1}{N} \log(P^N_{\boldsymbol{k}(\boldsymbol{s})}) + \frac{\beta}{\sqrt{N}} \sum_i s_i E_i \\ &\qquad + F^N_{\text{diss}} \geq 0 \text{ such that } \|\boldsymbol{s}\| \leq b \Big\}, \\ B(N) &:= \sum_{\boldsymbol{s}} \Big\{ P^N_{\boldsymbol{k}(\boldsymbol{s})} \Big| \frac{\beta}{\sqrt{N}} \sum_i s_i E_i + F^N_{\text{diss}} \geq 0 \Big\}, \\ B(b,N) &:= \sum_{\boldsymbol{s}} \Big\{ P^N_{\boldsymbol{k}(\boldsymbol{s})} \Big| \frac{\beta}{\sqrt{N}} \sum_i s_i E_i + F^N_{\text{diss}} \geq 0 \\ &\qquad \text{such that } \|\boldsymbol{s}\| \leq b \Big\}, \\ \Omega(b,N) &:= \sum_{\boldsymbol{s}} \Big\{ P^N_{\boldsymbol{k}(\boldsymbol{s})} \Big| \text{ such that } \|\boldsymbol{s}\| \geq b \Big\}. \end{aligned} \tag{6.52}$$

The aim is to show that

$$\lim_{N\to\infty} A(N) = \lim_{N\to\infty} B(N). \tag{6.53}$$

From the definition, it follows that

$$\begin{aligned} A(N) - \Omega(b,N) &\leq A(b,N) \leq A(N), && (6.54a)\\ B(N) - \Omega(b,N) &\leq B(b,N) \leq B(N). && (6.54b)\end{aligned}$$

In the limit $N \to \infty$ of Eqs. (6.54a) and (6.54b), we have

$$\begin{aligned} \lim_{N\to\infty}\Big(A(N) - \Omega(b,N)\Big) \leq \lim_{N\to\infty} A(b,N) \leq \lim_{N\to\infty} A(N), && (6.55a)\\ \lim_{N\to\infty}\Big(B(N) - \Omega(b,N)\Big) \leq \lim_{N\to\infty} B(b,N) \leq \lim_{N\to\infty} B(N). && (6.55b)\end{aligned}$$

Now, let us define

$$\lim_{N\to\infty} \Omega(b,N) =: \epsilon(b). \tag{6.56}$$

Since the multinomial distribution concentrates around mean for $N \to \infty$, it implies that $\lim_{b\to\infty} \epsilon(b) = 0$. Therefore, taking the limit $b \to \infty$ in Eq. (6.55a) we have

$$\begin{aligned} \lim_{N\to\infty} A(N) \leq \lim_{b\to\infty}\lim_{N\to\infty} A(b,N) \leq \lim_{N\to\infty} A(N)\\ \Rightarrow \quad \lim_{b\to\infty}\lim_{N\to\infty} A(b,N) = \lim_{N\to\infty} A(N). && (6.57)\end{aligned}$$

Similarly, taking the limit $b \to \infty$ in Eq. (6.55b) one can show that

$$\lim_{b\to\infty}\lim_{N\to\infty} B(b,N) = \lim_{N\to\infty} B(N). \tag{6.58}$$

Moreover, for any fixed b, by employing lemma 50, we are able to see that $\frac{1}{N}\log(P^N_{\boldsymbol{k}(\boldsymbol{s})}) = O(\frac{\log N}{N})$, which vanishes as $N \to \infty$. Therefore, we have

$$\lim_{N\to\infty} A(b,N) = \lim_{N\to\infty} B(b,N), \tag{6.59}$$

and so by taking the limit $b \to \infty$, we arrive at

$$\lim_{b\to\infty}\lim_{N\to\infty} A(b,N) = \lim_{b\to\infty}\lim_{N\to\infty} B(b,N). \tag{6.60}$$

Combining the above with Eqs. (6.57)-(6.58) we have

$$\lim_{N\to\infty} A(N) = \lim_{N\to\infty} B(N), \tag{6.61}$$

that completes the proof. □

6.5 Central limit theorem for multinomial distribution

Lemma 52. *The multinomial distribution with mean* $\boldsymbol{\mu} = N\boldsymbol{p}$ *and a covariance matrix* $\boldsymbol{\Sigma}$ *can be approximated in the asymptotic limit by a multivariate normal distribution* $\mathcal{N}^{(\boldsymbol{\mu},\boldsymbol{\Sigma})}$ *with mean* $\boldsymbol{\mu}$ *and a covariance matrix* $\boldsymbol{\Sigma}$*.*

Proof. Let us consider $\boldsymbol{X}_1 \dots \boldsymbol{X}_N$ are independent and identically distributed random vectors each of them with the following distribution

$$\mathrm{Prob}(\boldsymbol{X} = \boldsymbol{x}) = \begin{cases} \prod_{i=1}^{d} p_i^{x_i} & \text{if } \boldsymbol{x} \text{ is unit vector,} \\ 0 & \text{otherwise.} \end{cases} \tag{6.62}$$

Then, the mean vector of $\boldsymbol{X}$ is $\boldsymbol{p}$ and the covariance matrix $\frac{1}{N}\boldsymbol{\Sigma} =$ diag $(\boldsymbol{p}) - \boldsymbol{p}\boldsymbol{p}^T$. Define $\boldsymbol{S}_N := \boldsymbol{X}_1 + \dots + \boldsymbol{X}_N$. Then

$$\mathrm{Prob}(\boldsymbol{S}_N = \boldsymbol{k}) \quad = \quad \binom{N}{k_1 \dots k_d} p_1^{k_1} \dots p_d^{k_d}. \tag{6.63}$$

As a result, we can see that a multinomial distribution results from adding together random variables with independent and identical distributions. In order to conclude the proof, we use the central limit theorem to show that the distribution of vk approaches the distribution of $\mathcal{N}^{(\boldsymbol{\mu},\boldsymbol{\Sigma})}$ arbitrarily well for $N \to \infty$. ☐

6.6 Entropy difference between uniformised and non-uniformised embedding boxes

In this appendix, we would like to show the existence of a permutation that can convert the total final state $\hat{\boldsymbol{F}}^N$ from Eq. (3.99) into a state that is almost uniformly distributed in all embedding boxes. This results no dissipation up to higher-order asymptotics. The initial state comprises N independent systems in identical incoherent states $\boldsymbol{P}^N = \boldsymbol{p}^{\otimes N}$, and thus $\hat{\boldsymbol{P}}^N \otimes \hat{\tilde{\boldsymbol{G}}}^N$ has a polynomial number of distinct entries with exponential degeneracy and exponentially many embedding boxes. According to Eq. (3.99), the entries of $\hat{\boldsymbol{F}}^N$ are essentially given by the entries of $\hat{\boldsymbol{P}}^N \otimes \hat{\tilde{\boldsymbol{G}}}^N$, with additional equal entries $(1-\epsilon)/K$. Therefore, $\hat{\boldsymbol{F}}^N$ has polynomially many distinct entries with exponential degeneracy and exponentially many embedding boxes. By utilizing permutational freedom, we can rearrange the entries of $\hat{\boldsymbol{F}}^N$ to obtain a uniform distribution in almost every embedding box, except for poly(N) of them. The probability distribution over the embedding boxes, denoted by $\boldsymbol{q}$, is essentially equal to $\boldsymbol{P}^N \otimes, \tilde{\boldsymbol{G}}^N$, while the normalised distribution within the i-th embedding box is denoted by $\boldsymbol{r}^{(i)}$

To proceed further we write the entropy of the embedded total final state as the entropy of probability distribution over different embedding boxes, $H(\boldsymbol{q})$, plus the average entropy of normalised probabilities within each box, $H(\boldsymbol{r}^{(i)})$,

$$H(\hat{\boldsymbol{F}}^N) = H(\boldsymbol{q}) + \sum_i q_i H(\boldsymbol{r}^{(i)}). \tag{6.64}$$

Note that whether we uniformise or not a given box, the entropy $H(\boldsymbol{q})$ does not change. Consequently, the entropy of the final state uniformised within each embedding box takes the form of

$$H(\hat{\boldsymbol{F}}^N_{\mathrm{uni}}) = H(\boldsymbol{q}) + \sum_i q_i H(\boldsymbol{r}^{(i)}_{\mathrm{uni}}), \tag{6.65}$$

with $\boldsymbol{r}^{(i)}_{\mathrm{uni}}$ representing the normalised and uniformised probability within the i-th embedding box. Thus, the entropy difference between the uniformised and non-uniformised distributions reads

$$H(\hat{\boldsymbol{F}}^N_{\mathrm{uni}}) - H(\hat{\boldsymbol{F}}^N) = \sum_i q_i \left(H(\boldsymbol{r}^{(i)}_{\mathrm{uni}}) - H(\boldsymbol{r}^{(i)}) \right). \tag{6.66}$$

Now, note that due to the previous argument, the above sum is performed only over a polynomial number of boxes. Denoting the set with size poly(N) as Ω, one can write

$$\begin{aligned} H(\hat{\boldsymbol{F}}^N_{\mathrm{uni}}) - H(\hat{\boldsymbol{F}}^N) &= \sum_{i\in\Omega} q_i \left(H(\boldsymbol{r}^{(i)}_{\mathrm{uni}}) - H(\boldsymbol{r}^{(i)}) \right) \\ &\leq \sum_{i\in\Omega} q_i H(\boldsymbol{r}^{(i)}_{\mathrm{uni}}). \end{aligned} \tag{6.67}$$

Let us analyse the right-hand side of the above equation. First, note that q_i is exponentially small, $q_i \propto \exp(-N)$; while $H(\boldsymbol{r}^{(i)}_{\mathrm{uni}})$ is the entropy of a uniform state over the dimension of the i-th embedding box (equal to $\prod_i D_i^{k_i}$), so it will scale linearly in N:

$$H(\boldsymbol{r}^{(i)}_{\mathrm{uni}}) = \log \left(\prod_i D_i^{k_i} \right) \propto O(N). \tag{6.68}$$

Therefore, we conclude that the entropy difference vanishes exponentially in N

$$H(\hat{\boldsymbol{F}}^N_{\mathrm{uni}}) - H(\hat{\boldsymbol{F}}^N) \propto \exp(-N). \tag{6.69}$$

6.7 Proof of lemma 38

Let us start by rewriting the definition of the amount of heat exchanged with a hot reservoir given in Eq. (5.15) as follows:

$$Q(\mathcal{E}_H(\rho_S)) = \mathrm{Tr}(H_S(\mathcal{E}_H(\rho_S) - \rho_S)), \tag{6.70}$$

where ρ_S is the state of the working body that has been thermalized with cold reservoir at inverse temperature β_C as given in Eq. (5.8). We see that function $Q(\,\cdot\,)$ is linear. Therefore, when we minimise the function $Q(\,\cdot\,)$ over all the states that can be achieved from ρ_S via thermal operation i.e.,

$$\min_{\sigma_S \in \mathcal{T}(\rho_S)} Q(\sigma_S) := Q(\sigma_S^*), \tag{6.71}$$

where the minimum is achieved at an extremal point labelled by σ_S^* of the set $\mathcal{T}(\rho_S)$. Thus, to prove $Q(\sigma_S^*) \geq 0$, it suffices to show that $\sigma_S^* = \rho_S$. According to definition 35, applying a thermal operation on the state ρ_S in the presence of a hot bath at inverse temperature β_H is equivalent to applying a Gibbs stochastic matrix on the classical state $\boldsymbol{p}_S$, where

$$\boldsymbol{p}_S = \Big(\langle E_1|\rho_S|E_1\rangle \ldots \langle E_d|\rho_S|E_d\rangle\Big). \tag{6.72}$$

This Gibbs stochastic matrix preserves the classical state $\boldsymbol{\gamma}_{\beta_H}$ where $\boldsymbol{\gamma}_{\beta_H}$ is given as

$$\boldsymbol{\gamma}_{\beta_H} = \Big(\frac{e^{-\beta E_1}}{Z} \ldots \frac{e^{-\beta E_d}}{Z}\Big) \quad \text{where} \quad Z = \sum_{i=1}^{d} e^{-\beta E_i}. \tag{6.73}$$

. Note that the classical state $\boldsymbol{p}_S$ has β-order $(12\ldots d)$ with respect to $\boldsymbol{\gamma}_{\beta_H}$. From definition of future thermal cone $\mathcal{T}(\rho_S)$, we see that $(\boldsymbol{p}_S, \boldsymbol{\gamma}_{\beta_H}) \succ (\boldsymbol{s}_S^*, \boldsymbol{\gamma}_{\beta_H})$ where

$$\boldsymbol{s}_S^* = \Big(\langle E_1|\sigma_S^*|E_1\rangle \ldots \langle E_d|\sigma_S^*|E_d\rangle\Big). \tag{6.74}$$

If $\boldsymbol{s}_S^*$ has β-order $(12\ldots d)$ then using lemma 37, immediately gives $\boldsymbol{s}_S^* = \boldsymbol{p}_S$. Now consider the situation when $\boldsymbol{s}_S^*$ has β-order $(\alpha_1 \ldots \alpha_d) \neq (12\ldots d)$. Then, there will be at least two consecutive entries α_k and α_l in the β-order $(\alpha_1 \ldots \alpha_d)$ such that $\alpha_k > \alpha_l$. Let us call $\alpha_k = i$ and $\alpha_l = j$ where i , $j \in \{1, \ldots, d\}$. Since $i > j$, therefore $\epsilon_i > \epsilon_j$ since conventionally we take $E_1 \leq E_2 \leq \ldots E_d$. Now we shall construct the following stochastic matrix

$$\mathcal{A} = \begin{pmatrix} 1 - e^{-\beta_H(E_i - E_j)} & 1 \\ e^{-\beta_H(E_i - E_j)} & 0 \end{pmatrix} \oplus \mathbb{I}_{\text{Rest}}, \tag{6.75}$$

where $\mathbb{I}_{\text{Rest}}$ is the identity matrix on the subspace orthogonal to the subspace spanned by $\{|E_i\rangle, |E_j\rangle\}$. It is easy to see that $\mathcal{A}(\gamma_{\beta_H}) = \gamma_{\beta_H}$. Next, from the definition of β-order, we can write

$$\frac{\langle E_i|\sigma_S^*|E_i\rangle}{e^{-\beta_H E_i}} > \frac{\langle E_j|\sigma_S^*|E_j\rangle}{e^{-\beta_H E_j}}, \tag{6.76}$$

since $i = \alpha_k$ appears before $j = \alpha_l$ in the β-order $(\alpha_1 \ldots \alpha_d)$. Note that we can always choose α_k and α_l in such a way that Eq. (6.76) is a strict inequality. If it is not true, this will lead us to conclude that $\boldsymbol{s}_S^* = \gamma_{\beta_H}$ which is not the case, because σ_S^* has to be the extremal point of $\mathcal{T}(\rho_S)$. From Eq. (6.76) we have,

$$\langle \epsilon_i|\sigma_S^*|E_i\rangle > \langle E_j|\sigma_S^*|E_j\rangle e^{-\beta_H(E_i - E_j)}, \tag{6.77}$$

Applying the stochastic matrix $\mathcal{A}$ to the initial classical state $\boldsymbol{s}S^*$ results in the transformation of the probabilities for the energy levels $|E_j\rangle$ and $|E_i\rangle$, given by

$$\begin{aligned}
(\mathcal{A}\boldsymbol{s}_S^*)j &= (\langle E_j|\sigma_S^*|E_j\rangle + \langle E_i|\sigma_S^*|E_i\rangle) - \langle E_j|\sigma_S^*|E_j\rangle e^{-\beta_H(E_i - E_j)}, & (6.78)\\
(\mathcal{A}\boldsymbol{s}_S^*)i &= \langle E_j|\sigma_S^*|E_j\rangle e^{-\beta_H(E_i - E_j)}, & (6.79)
\end{aligned}$$

while leaving the probabilities of other energy levels unchanged. Since $E_i > E_j$, using Eq. (6.77), the resulting state has a strictly lower average energy than σ_S^*. In other words, using the Gibbs stochastic matrix $\mathcal{A}$, which acts non-trivially only on the energy levels $|E_i\rangle$ and $|E_j\rangle$, we have decreased the population of the higher energy level $|E_i\rangle$, and increased the population of the lower energy level $|E_j\rangle$. This implies that the state with diagonal entries given by $\mathcal{A}\boldsymbol{s}_S^*$ has strictly less energy than σ_S^*. This contradicts the assumption that σ_S^* is the state with the lowest energy in the set $\mathcal{T}(\rho_S)$, and thus we conclude that σ_S^* must be equal to ρ_S.

6.8 Detailed analysis of open cycle heat engine with qutrit working body.

This section provides a comprehensive computation of the amount of ergotropy obtainable from the hot bath using the initial state ρ_S. The state, denoted by ρ_S, is given by

$$\rho_S = |0\rangle\langle 0| + q_{10}^C|1\rangle\langle 1| + q_{20}^C|2\rangle\langle 2|, \quad \text{where} \quad Z_C = 1 + q_{10}^C + q_{20}^C \tag{6.80}$$

and q_{ij}^C is defined in Eq. (5.32) as $q_{ij}^C = e^{-\beta_C(\omega_i - \omega_j)}$. The classical state obtained from the diagonal of $\hat{\rho}S$ is expressed as

$$\boldsymbol{p}S = \frac{1}{Z_C}(1 \quad q_{10}^C \quad q_{20}^C), \tag{6.81}$$

where Z_C is the normalization constant. The β-order of $\boldsymbol{p}_S$ at inverse temperature β_H can be determined from the inequality

$$\frac{1}{Z_C} \geq \frac{q_{10}^C}{e^{-\beta_H \omega_1}} \geq \frac{q_{20}^C}{e^{-\beta_H \omega_2}}, \tag{6.82}$$

which implies that the β-order is (123).

We will employ the lemma from [157] to describe the extreme Gibbs stochastic matrixes that operate on a classical state $\boldsymbol{p}$ having a β-order of (123) and provide the spectrum of the resulting extremal states of $\mathcal{T}(\rho_S)$.

Lemma 2. *[Based on table 1 of [157]] For the inverse temperature β_H, the Gibbs stochastic matrices that produce the spectrum of non-trivial extremal states in $\mathcal{T}(\rho_S)$ for a classical state $\mathbf{p}$ having a β-order of (123) are described by the following:*

$$\begin{cases} A_1, A_2, A_5, A_9 & \text{for } \beta_H \geq \beta_0, \\ A_1, A_2, A_5, A_{12}, A_{13} & \text{for } \beta_H < \beta_0, \end{cases} \tag{6.83}$$

where β_0 is determined by the following equality

$$e^{-\beta_0 \omega_1} + e^{-\beta_0 \omega_2} = 1, \tag{6.84}$$

and

$$A_1 = \begin{pmatrix} 1 - q_{10}^H & 1 & 0 \\ q_{10}^H & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad A_2 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 - q_{21}^H & 1 \\ 0 & q_{21}^H & 0 \end{pmatrix}, \tag{6.85}$$

$$A_5 = \begin{pmatrix} 1 - q_{20}^H & q_{21}^H & 0 \\ 0 & 1 - q_{21}^H & 1 \\ q_{20}^H & 0 & 0 \end{pmatrix} \qquad A_9 = \begin{pmatrix} 1 - q_{10}^H - q_{20}^H & 1 & 1 \\ q_{10}^H & 0 & 0 \\ q_{20}^H & 0 & 0 \end{pmatrix}, \tag{6.86}$$

$$A_{12} = \begin{pmatrix} 0 & q_{01}^H - q_{21}^H & 1 \\ q_{10}^H & 0 & 0 \\ 1 - q_{10}^H & 1 - q_{01}^H + q_{21}^H & 0 \end{pmatrix} \qquad A_{13} = \begin{pmatrix} 0 & q_{01}^H - q_{21}^H & 1 \\ 1 - q_{20}^H & 1 - q_{01}^H + q_{21}^H & 0 \\ q_{20}^H & 0 & 0 \end{pmatrix} \tag{6.87}$$

The final β-order of the Gibbs stochastic matrix in Eq. (6.83) for a classical state with a β-order of (123) is given by:

Gibbs stochastic matrixes	β*-order*
A_1	*(213)*
A_2	*(132)*
A_5	*(312)*
A_9	*(231) or (321)*
A_{12}	*(231)*
A_{13}	*(321)*

By applying this lemma, we will examine the most efficient operation of an open-cycle heat engine that has an initial state with a spectrum of $\boldsymbol{p}_S$, which involves determining the maximum ergotropy that can be extracted from the hot bath through Gibbs stochastic matrix A_i and storing it as work. We will refer to this quantity as $R_{A_i}(\boldsymbol{p}_S)$ and use it to calculate the engine's efficiency.

Using Gibbs stochastic matrix A_1, the amount of heat transferred from the hot bath and the extractable ergotropy from $\boldsymbol{p}_S$ can be calculated as follows :

The Gibbs stochastic matrix A_1 transforms the initial classical state given in Eq. (6.81) in the following manner:

$$\frac{1}{Z_C}\begin{pmatrix}1-q^H_{10} & 1 & 0\\ q^H_{10} & 0 & 0\\ 0 & 0 & 1\end{pmatrix}\begin{pmatrix}1\\ q^C_{10}\\ q^C_{20}\end{pmatrix} = \frac{1}{Z_C}\begin{pmatrix}(1-q^H_{10})+q^C_{10}\\ q^H_{10}\\ q^C_{20}\end{pmatrix} = \text{Spec}(\rho^1_S), \tag{6.88}$$

Table 2 provides us with the β-order of the final classical state in Eq. (6.88), which is (213). Thus,

$$\begin{aligned} &\frac{q^H_{10}}{Z_C q^H_{10}} \geq \frac{(1-q^H 10)+q^C 10}{Z_C} \geq \frac{q^C_{20}}{Z_C q^H_{20}} \\ \Rightarrow\ & (1-q^H 10)+q^C 10 \geq \frac{q^C_{20}}{q^H_{20}} \geq q^C_{20}, \end{aligned} \tag{6.89}$$

where the final inequality follows from the relation that $0 \leq q^H_{20} \leq 1$. Hence, the population order that satisfies Eq. (6.89) can be expressed as follows:

$$\frac{(1-q^H 10)+q^C 10}{Z_C} \geq \frac{q^H_{10}}{Z_C} \geq \frac{q^C_{20}}{Z_C}, \tag{6.90}$$

$$\frac{q^H_{10}}{Z_C} \geq \frac{(1-q^H 10)+q^C 10}{Z_C} \geq \frac{q^C_{20}}{Z_C}. \tag{6.91}$$

If the population order is given by Eq. (6.90), then the final state is passive, and no ergotropy can be extracted from it. On the other hand, if the order of the population in the final classical state given by Eq. (6.88) satisfies Eq. (6.91), the amount of ergotropy that can be extracted is given by

$$\begin{aligned}R_{A_1}(\boldsymbol{p}_S) &= \max\left\{0, \frac{\omega_1}{Z_C}\Big(2q_{10}^H - 1 - q_{10}^C\Big)\right\} \\ &= \max\left\{0, \frac{\omega_1}{Z_C}(2q_{10}^H - 1 - q_{10}^C)\right\}. \qquad (6.92)\end{aligned}$$

Therefore, positive extraction of ergotropy is possible if

$$2q_{10}^H \geq 1 + q_{10}^C. \qquad (6.93)$$

Using Gibbs stochastic matrix A_2, the amount of heat transferred from the hot bath and the extractable ergotropy from $\boldsymbol{p}_S$ can be calculated as follows : The Gibbs stochastic matrix A_2 transforms the initial classical state given in Eq. (6.81) in the following manner:

$$\frac{1}{Z_C}\begin{pmatrix}1 & 0 & 0\\ 0 & 1-q_{21}^H & 1\\ 0 & q_{21}^H & 0\end{pmatrix}\begin{pmatrix}1\\ q_{10}^C\\ q_{20}^C\end{pmatrix} = \frac{1}{Z_C}\begin{pmatrix}1\\ (1-q_{21}^H)q_{10}^C + q_{20}^C\\ q_{21}^H q_{10}^C\end{pmatrix} = \mathrm{Spec}(\rho_S^2). \qquad (6.94)$$

Table 2 provides us with the β-order of the final classical state in Eq. (6.88), which is (132). Thus,

$$\begin{aligned}\frac{1}{Z_C} &\geq \frac{q_{21}^H q_{10}^C}{Z_C q_{20}^H} \geq \frac{(1-q_{21}^H)q_{10}^C + q_{20}^C}{Z_C q_{10}^H}, \qquad (6.95)\\ \Rightarrow\quad 1 &\geq q_{21}^H q_{10}^C \quad \text{and} \quad 1 \geq (1-q_{21}^H)q_{10}^C + q_{20}^C,\end{aligned}$$

where the final inequality follows from the relation that $0 \leq q_{20}^H \leq 1$. Hence, the population order that satisfies Eq. (6.95) can be expressed as follows:

$$\frac{1}{Z_C} \geq \frac{(1-q_{21}^H)q_{10}^C + q_{20}^C}{Z_C} \geq \frac{q_{21}^H q_{10}^C}{Z_C}, \qquad (6.96)$$

$$\frac{1}{Z_C} \geq \frac{q_{21}^H q_{10}^C}{Z_C} \geq \frac{(1-q_{21}^H)q_{10}^C + q_{20}^C}{Z_C}, \qquad (6.97)$$

If the population order of the final classical state in Equation (6.94) follows Equation (6.96), then the final classical state is passive and no ergotropy can be extracted. The amount of ergotropy that can be extracted from the final classical state using thermal operation A_2 is determined by Equation:

$$R_{A_2}(\boldsymbol{p}_S) = \max\left\{0, \frac{1}{Z_C}(\omega_2 - \omega_1)\Big(2q_{21}^H q_{10}^C - (q_{10}^C + q_{20}^C\Big)\right\}. \qquad (6.98)$$

Thus, a condition for positive ergotropy extraction can be expressed as:

$$2q_{21}^{H} \geq 1 + q_{21}^{C}. \tag{6.99}$$

Using Gibbs stochastic matrix A_5, the amount of heat transferred from the hot bath and the extractable ergotropy from $\boldsymbol{p}_S$ can be calculated as follows: The Gibbs stochastic matrix A_5 transforms the initial classical state given in Eq. (6.81) in the following manner:

$$\frac{1}{Z_C}\begin{pmatrix} 1-q_{20}^{H} & q_{21}^{H} & 0 \\ 0 & 1-q_{21}^{H} & 1 \\ q_{20}^{H} & 0 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ q_{10}^{C} \\ q_{20}^{C} \end{pmatrix} = \frac{1}{Z_C}\begin{pmatrix} 1-q_{20}^{H}+q_{21}^{H}q_{10}^{C} \\ (1-q_{21}^{H})q_{10}^{C}+q_{20}^{C} \\ q_{20}^{H} \end{pmatrix} = \mathrm{Spec}(\rho_S^3) \tag{6.100}$$

Table 2 provides us with the β-order of the final classical state in Eq. (6.100), which is (312). Thus, it means

$$\begin{aligned} &\frac{q_{20}^{H}}{Z_C q_{20}^{H}} \geq \frac{1-q_{20}^{H}+q_{21}^{H}q_{10}^{C}}{Z_C} \geq \frac{(1-q_{21}^{H})q_{10}^{C}+q_{20}^{C}}{Z_C q_{10}^{H}}, \\ \Rightarrow\ &(1-q_{21}^{H})q_{10}^{C}+q_{20}^{C} \geq (1-q_{21}^{H})q_{10}^{C}+q_{20}^{C}, \end{aligned} \tag{6.101}$$

where we write the final inequality using the relation $0 \leq q_{10}^{H} \leq 1$. The order of populations compatible with Eq. (6.101) is determined by:

$$\frac{1-q_{20}^{H}+q_{21}^{H}q_{10}^{C}}{Z_C} \geq \frac{(1-q_{21}^{H})q_{10}^{C}+q_{20}^{C}}{Z_C} \geq \frac{q_{20}^{H}}{Z_C}, \tag{6.102}$$

$$\frac{1-q_{20}^{H}+q_{21}^{H}q_{10}^{C}}{Z_C} \geq \frac{q_{20}^{H}}{Z_C} \geq \frac{(1-q_{21}^{H})q_{10}^{C}+q_{20}^{C}}{Z_C}, \tag{6.103}$$

$$\frac{q_{20}^{H}}{Z_C} \geq \frac{1-q_{20}^{H}+q_{21}^{H}q_{10}^{C}}{Z_C} \geq \frac{(1-q_{21}^{H})q_{10}^{C}+q_{20}^{C}}{Z_C}. \tag{6.104}$$

If the population order for the final classical state in Eq. (6.100) follows Eq. (6.102), no ergotropy can be extracted as the final classical state is already passive. Non-trivial ergotropy extraction is possible if the ordering is given by Eqs. (6.103) and (6.104). The amount of extractable ergotropy is calculated by:

$$\begin{aligned} R_{A_5}(\boldsymbol{p}_S) \;=\; \max\Big\{0,\ &\frac{(\omega 2-\omega_1)}{Z_C}\Big(q_{20}^{H}-q_{20}^{C}-(1-q_{21}^{H})q_{10}^{C}\Big),\ \frac{\omega 2}{Z_C}q_{20}^{H} \\ &-\frac{\omega 1}{Z_C}\Big((1-q_{20}^{H})+q_{21}^{H}q_{10}^{C}\Big)-\frac{(\omega 2-\omega_1)}{Z_C}\Big((1-q_{21}^{H})q_{10}^{C}+q_{20}^{C}\Big)\Big\}. \end{aligned} \tag{6.105}$$

Using Gibbs stochastic matrix A_9, the amount of heat transferred from the hot bath and the extractable ergotropy from $\boldsymbol{p}_S$ can be calculated as follows: The Gibbs stochastic matrix A_9 transforms the initial classical state given in Eq. (6.81) in the following manner:

$$\frac{1}{Z_C}\begin{pmatrix} 1-q^H_{10}-q^H_{20} & 1 & 1 \\ q^H_{10} & 0 & 0 \\ q^H_{20} & 0 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ q^C_{10} \\ q^C_{20} \end{pmatrix} = \frac{1}{Z_C}\begin{pmatrix} 1+q^C_{10}+q^C_{20}-q^H_{10}-q^H_{20} \\ q^H_{10} \\ q^H_{20} \end{pmatrix} = \mathrm{Spec}(\rho^4_S). \tag{6.106}$$

As $q^H_{10} \geq q^H_{20}$ holds for any plausible values of β_H, the possible population orders are given by

$$\frac{1+q^C_{10}+q^C_{20}-q^H_{10}-q^H_{20}}{Z_C} \geq \frac{q^H_{10}}{Z_C} \geq \frac{q^H_{20}}{Z_C}, \tag{6.107}$$

$$\frac{q^H_{10}}{Z_C} \geq \frac{1+q^C_{10}+q^C_{20}-q^H_{10}-q^H_{20}}{Z_C} \geq \frac{q^H_{20}}{Z_C}, \tag{6.108}$$

$$\frac{q^H_{10}}{Z_C} \geq \frac{q^H_{20}}{Z_C} \geq \frac{1+q^C_{10}+q^C_{20}-q^H_{10}-q^H_{20}}{Z_C}. \tag{6.109}$$

If the population order in the final classical states is described by Eq. (6.107), then no ergotropy extraction is possible since the initial state is already passive. However, non-trivial ergotropy extraction becomes feasible when the population order in the final classical state given by Eq. (6.106) satisfies Eq. (6.108) and Eq. (6.109). Hence, the amount of extractable ergotropy can be determined by

$$\begin{aligned} R_{A_9}(\boldsymbol{p}_S) &= \max\Big\{0, \frac{\omega 1}{Z_C}\Big(2q^H_{10}+q^H_{20}-(1+q^C_{10}+q^C_{20})\Big), \\ &\quad \frac{\omega_1}{Z_C}(q^H_{10}-q^H_{20}) + \frac{\omega_2}{Z_C}\Big(2q^H_{20}+q^H_{10}-(1+q^C_{10}+q^C_{20})\Big)\Big\}. \end{aligned} \tag{6.110}$$

Using Gibbs stochastic matrix A_{12}, the amount of heat transferred from the hot bath and the extractable ergotropy from $\boldsymbol{p}_S$ can be calculated as follows: The Gibbs stochastic matrix A_{12} transforms the initial classical state given in Eq. (6.81) in the following manner:

$$\frac{1}{Z_C}\begin{pmatrix} 0 & q^H_{01}-q^H_{21} & 1 \\ q^H_{10} & 0 & 0 \\ 1-q^H_{10} & 1-q^H_{01}+q^H_{21} & 0 \end{pmatrix}\begin{pmatrix} 1 \\ q^C_{10} \\ q^C_{20} \end{pmatrix} = \frac{1}{Z_C}\begin{pmatrix} (q^H_{01}-q^H_{21})q^C_{10}+q^C_{20} \\ q^H_{10} \\ (1-q^H_{10})+(1-q^H_{01}+q^H_{21})q^C_{10} \end{pmatrix} = \mathrm{Spec}(\rho^5_S), \tag{6.111}$$

We can see from the table 2, the β- order of the final classical state in Eq. (6.111) is (231).

That implies

$$\begin{aligned}
\frac{q^H_{10}}{Z_C q^H_{10}} &\geq \frac{(1-q^H_{10}) + (1-q^H_{01}+q^H_{21})q^C_{10}}{Z_C q^H_{20}} \\
&\geq \frac{(q^H_{01}-q^H_{21})q^C_{10}+q^C_{20}}{Z_C} \\
&\Rightarrow q^H_{10} \geq \frac{q^H_{10}}{q^H_{20}}(1-q^H_{10}) + (1-q^H_{01}+q^H_{21})q^C_{10} \\
&\geq (1-q^H_{10}) + (1-q^H_{01}+q^H_{21})q^C_{10},
\end{aligned} \tag{6.112}$$

where the final inequality follows from the relation $q^H_{10} \geq q^H_{20}$. Hence the ordering of the populations of the final classical state Eq. (6.111) that are compatible with Eq. (6.112) is given by

$$\frac{1}{Z_C}\Big((q^H_{01}-q^H_{21})q^C_{10}+q^C_{20}\Big) \geq \frac{q^H_{10}}{Z_C} \geq \frac{1}{Z_C}\Big((1-q^H_{10}) + (1-q^H_{01}+q^H_{21})q^C_{10}\Big), \tag{6.113}$$

$$\frac{q^H_{10}}{Z_C} \geq \frac{1}{Z_C}\Big((q^H_{01}-q^H_{21})q^C_{10}+q^C_{20}\Big) \geq \frac{1}{Z_C}\Big((1-q^H_{10}) + (1-q^H_{01}+q^H_{21})q^C_{10}, \tag{6.114}$$

$$\frac{q^H_{10}}{Z_C} \geq \frac{1}{Z_C}\Big((1-q^H_{10}) + (1-q^H_{01}+q^H_{21})q^C_{10}\Big) \geq \frac{1}{Z_C}\Big((q^H_{01}-q^H_{21})q^C_{10}+q^C_{20}\Big), \tag{6.115}$$

If the population ordering of the final classical state in Eq. (6.111) is described by Eq. (6.113), ergotropy extraction is not possible due to the passivity of the initial state. Hence, non-trivial ergotropy extraction can only occur if the ordering of the populations in the final classical state is governed by Eq. (6.114) or Eq. (6.115). The amount of ergotropy that can be extracted using thermal operation A_{12} is given by

$$\begin{aligned}
R_{A_{12}}(\boldsymbol{p}_S) = \max\Big\{&0, \frac{\omega_1}{Z_C}\Big(q^H_{10} - (q^H_{01}-q^H_{21})q^C_{10} - q^C_{20}\Big), \frac{\omega_1}{Z_C}\Big(q^H_{10} - (1-q^H_{10}) - (1-q^H_{01}-q^H_{21})q^C_{10}\Big) \\
&+\frac{\omega_2}{Z_C}\Big((1-q^H_{10}) + (1-q^H_{01}-q^H_{21})q^C_{10} - (q^H_{01}-q^H_{21})q^C_{10} - q^C_{20}\Big)\Big\}.
\end{aligned} \tag{6.116}$$

Using Gibbs stochastic matrix A_{13}, the amount of heat transferred from the hot bath and the extractable ergotropy from p_S can be calculated as follows: The Gibbs stochastic matrix A_{13} transforms the initial classical state given in Eq. (6.81) as follows

$$\frac{1}{Z_C}\begin{pmatrix} 0 & q^H_{01}-q^H_{21} & 1 \\ 1-q^H_{20} & 1-q^H_{01}+q^H_{21} & 0 \\ q^H_{20} & 0 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ q^C_{10} \\ q^C_{20} \end{pmatrix} = \frac{1}{Z_C}\begin{pmatrix} q^C_{10}(q^H_{01}-q^H_{21})+q^C_{20} \\ 1-q^H_{20}+q^C_{10}(1-q^H_{01}+q^H_{21}) \\ q^H_{20} \end{pmatrix} = \mathrm{Spec}(\rho^6_S), \tag{6.117}$$

Based on table 2, we observe that the β-ordering of the final classical state corresponds to (321). It is evident that any ordering of the populations in the final classical state described by Eq. (6.117) is consistent with this β-order. Thus ergotropy can be calculated as

$$\begin{aligned}
R_{A_{13}}(\boldsymbol{p}_S) &= \max\Bigg\{0, \frac{\omega_2-\omega_1}{Z_C}\Big(2q_{20}^H - 1 - q_{10}^C\Big(1+q_{21}^H-q_{01}^H\Big)\Big),\ \frac{\omega_1}{Z_C}\Big(1-q_{20}^C-q_{20}^H \\
&+ q_{10}^C\Big(1+2q_{21}^H-2q_{01}^H\Big)\Big),\ \frac{\omega_1}{Z_C}\Big(q_{10}^C\Big(1+q_{21}^H-q_{01}^H\Big)+1-2q_{20}^H\Big)+\frac{\omega_2}{Z_C}\Big(q_{20}^H-q_{20}^C \\
&+ q_{10}^C q_{21}^H - q_{10}^C q_{01}^H\Bigg),\ \frac{\omega_1}{Z_C}\Big(1-q_{20}^C-q_{20}^H+q_{10}^C\Big(1+2q_{21}^H-2q_{01}^H\Big)\Big)-\frac{\omega_2}{Z_C}\Big(1-2q_{20}^H \\
&+ q_{10}^C\Big(1+q_{21}^H-q_{01}^H\Big)\Big),\ \frac{\omega_2}{Z_C}\Big(q_{20}^H-q_{20}^C+q_{10}^C\Big(q_{21}^H-q_{01}^H\Big)\Big)\Bigg\}. \qquad (6.118)
\end{aligned}$$

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