

Work, Heat, and Power of Quantum Processes



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A thesis submitted for the degree of
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Abstract

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The central purpose of this thesis is to study the familiar processes of quantum information theory from a thermodynamic point of view.

Chapter 1 introduces equilibrium thermodynamics and its laws. The laws are then motivated in a statistical mechanics approach which explicitly employs the language of quantum information theory.

Chapter 2 is dedicated to the concept of work extraction, in particular in non-equilibrium scenarios. In this context a generalised notion of equilibrium called passivity is introduced. The chapter's final section gives an introduction and an overview of various approaches to work extraction ranging from classical to explicitly quantum scenarios.

Chapter 3 considers the question of powerful unitary operations. Focussing on the case of qubits (or rather wits, short for 'work bits') the chapter's first result is an explicit protocol for maximally powerful driving for any given initial state. Building onto this, the chapter's second main result is a proof that the evolution time (and hence the power of the corresponding work deposition process) can be decreased by a factor of $1/N$ for an array of N wits if global driving is permitted (rather than individual driving in parallel).

Lastly, the thermodynamics of completely-positive and trace-preserving (CPTP) maps is considered in Chapter 4. It is shown that the energy change during such a process can be split into three parts: a work-like equilibrium contribution, a heat-like equilibrium contribution, and a third genuinely non-equilibrium energy difference. All three terms obtain their meaning when considering how much work can be extracted from the input and output state of the CPTP process, respectively. Furthermore, the identification of work and heat in this manner complies with a recently published version of the second law, which applies to the same class of processes. This is demonstrated by considering unital and thermal maps.

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A mindset of inquisitiveness seems to run in the family. I want to deeply thank my parents and my brother Clemens not only for their unwavering support but also for always encouraging critical thought and sharing the joy of learning. Last but not least, I am immensely grateful to Shreya Atrey who is as loving a partner, as supportive a friend, and as thoughtful an intellectual sparring partner, I could hope for.

Preface

This thesis is a study of thermodynamics from a quantum operational perspective. The central inquiry is how thermodynamic quantities like work, heat, and power may be meaningfully ascribed to the familiar processes of quantum information theory, such as unitary and completely-positive and trace-preserving (CPTP) channels. And, with such a description in mind, what are the thermodynamic advantages (and disadvantages) due to quantum effects?

In addressing this inquiry we go beyond the limits of thermodynamic equilibrium, unbounded system size and unbounded process duration. In order to do so, an operational mindset is employed throughout – not only by considering various types of evolution (in general: quantum operations) but also by implicitly assuming an experimental setting that allows for state preparation, (some level of) system control, and measurement. Crucially, as so often, the fine details are important: when talking about operational thermodynamics we have to be precise about the ‘rules of the game’. For instance, the question of how much work may be extracted from an out-of-equilibrium quantum state can only be answered in relation to a clear specification of what constraints apply to the implicitly assumed experimenter.

Quantum theory possesses some puzzling features that have been the focal point of research since the inception of the theory. Particular attention has been devoted to the phenomenon of quantum coherence (recently spiking interest, for instance, in the emerging field of quantum biology [Arndt et al., 2009; Mohseni et al., 2014]). Equally, quantum correlations – entanglement and the more recent notion of quantum discord [Henderson and Vedral, 2001; Ollivier and Zurek, 2002; Modi et al., 2012] – have been widely investigated in a diverse range of contexts since their first, and now famous, study by Einstein, Podolsky, and Rosen (EPR) [1935]. These two phenomena – quantum coherence and quantum correlations – are in fact two of the fundamental topics of study in the relatively young discipline which is quantum information science [Nielsen and Chuang, 2000]. This field, associated with quantum technologies such as quantum computers and quantum cryptography, has actively driven investigations, developing fruitful perspectives with a mindset directly inspired by and based on information theory and informatics. Quantum computers have become commercially available in recent years and their existence and use has gained media attention fuelled not least by collaborations between Google, NASA, Lockheed Martin, and D-Wave (the developer and producer of a specific type of quantum computer). Applications of quantum cryptography, albeit enjoying less popular attention, have arguably reached even higher commercial maturity. In spite of these commercial successes, fundamental research about basic quantum properties such as entanglement and their role in the technological advantage of quantum devices continues.

Quantum computation for instance is known to yield a significant speedup over classical computation for certain computational tasks. Shor’s algorithm, which can efficiently factorise large numbers, and Grover’s algorithm, which allows for efficient searching of a database, are popular examples of the advantage which quantum computation seems to have over its non-quantum, conventional counterparts [Shor, 1994; Grover, 1996; Ekert et al., 2000]. In this context, a ‘speedup’ is understood as an ad-

vantageous scaling of resource use (i.e., storage) and/or the number of basic operations necessary to perform a certain task with the size of the input into the computation (for instance, the number of digits in a number that is to be factorised). Interestingly, it is still debated which physical property causes the enhancement of quantum operations. This is exemplified by the discussion about the deterministic-quantum-computation-with-one-quantum-bit (DQC1) model of quantum computation [Knill and Laflamme, 1998]. Albeit not being universal, this model draws into question the common perception that it is quantum entanglement built up during the computation which allows some quantum algorithms to outperform their classical analogues [Datta et al., 2008].

From a different perspective it has been demonstrated that, while advantages may arise from quantum technology, the further miniaturisation of computers also faces fundamental hurdles due to an unexpected cause: Landauer [1961] famously showed that the erasure of information (i.e., a resetting of a bit in a computer) leads to the dissipation of heat, hence establishing a strong connection between thermodynamics and information theory.

As technological development enters into ever smaller realms it will be crucial to not only gain a profound understanding of the capabilities of future computation technologies (such as quantum computers) but also of their energetics. Fundamental phenomena like Landauer heat, the influence of disorder on transport processes, and quantum effects in energy storage may impose hurdles but can also open up technological opportunities for the field of quantum computation and beyond.

This thesis is in fact concerned with a topic that hinges on the same phenomena as quantum computation. It aims to shed light on what qualities make quantum processes powerful by embracing a thermodynamic point of view. A quantum perspective on thermodynamics will be outlined in Chapter 1 which is followed by a consideration of work extraction in Chapter 2. Chapter 3's main concern is the question of (thermo-

dynamic) power in quantum processes. It combines the study of coherence (in work extraction) with that of a quantum speedup (here, in the literal sense of taking less time T to perform a task, i.e., charging a battery). As it turns out, quantum correlations have a rather direct and significant impact on the optimised process duration T . Chapter 4 then further elucidates the role of quantum non-equilibrium – exemplified by population inversion and coherence with respect to an energy reference – in characterising the thermodynamic qualities of quantum operations (or, synonymously, CPTP channels).

Both of these chapters present original research and the main results have been published in scientific journals [Binder et al., 2015a,b]. All original research papers are also available on the online preprint-archive arxiv.org. Some of the results presented in this thesis go significantly beyond and extend the findings of these existing publications. This will be highlighted at appropriate places. The box below summarises the main results presented in this thesis. It is followed by a brief overview of the structure of the thesis and a short notational guide.

Main results

- An analytical, precise protocol for powerful unitary qubit driving under external constraints (Chapter 3);
- An analysis of global driving for an array of qubits, demonstrating significant improvements over the single qubit case (Chapter 3);
- An operational first-law-like relation: assignment of work, heat, and a third genuine out-of-equilibrium term that holds even in absence of assumptions like weak coupling (Chapter 4).

Overview

In Chapter 1, (quantum) thermodynamics will be presented in a didactic fashion and from a broad perspective in order to provide an appropriate context for the research presented in the following chapters. This chapter does not aim to give a complete overview of the overlap between thermodynamics and quantum information theory. The reader is instead directed to the recent topical reviews by Goold et al. [2015] and Vinjanampathy and Anders [2015], and references therein. Rather, we focus on providing the necessary context for the following chapters based on the canonical laws of thermodynamics.

Chapter 1 as well as the rest of this thesis, should be accessible to any physicist at the postgraduate level with some knowledge of the basic tools of quantum information theory. We presume that the reader is familiar with the concepts covered in the book by Nielsen and Chuang [2000], such as the density operator formalism, qubits and their representation on the Bloch Sphere, quantum channels, entropy, etc. In order to avoid notational ambiguity and provide maximal self-containment, some relevant, brief definitions are provided in Appendix B. The reader is referred to Nielsen and Chuang [2000] for a didactic introduction to quantum information theory. Some further references to books and review articles are made throughout the text where appropriate.

Chapter 2 reviews the concept of unitary work extraction. The notion of passivity is introduced and it is shown how the form of thermal states can be derived ‘bottom-up’ – that is, from simple, microscopic axioms. Based on this idea of passivity we introduce the concept of ergotropy – the maximum work that can be gained from a quantum state ρ with respect to some reference Hamiltonian H under cyclic unitary evolution. This chapter concludes with some remarks on the role of quantum correlations in unitary work extraction and the relationship to other frameworks such as thermal operations is discussed.

In Chapter 3, we study the maximum power that a quantum process can achieve with respect to a reference Hamiltonian and in the presence of some external bound on the driving. An explicit protocol for single-qubit driving is developed and presented. In a second step, we compare the optimal power of a single-qubit operation to an operation that globally acts on an array of N qubits. A significant improvement in power per qubit, linear in N , is shown in the global case.

Chapter 4 addresses the question of assigning notions of work and heat to more general quantum processes than unitary evolution. Importantly, no assumption of weak coupling is made. A priori it is clear that in such a setting one cannot hope to recover the conventional expressions for work and heat which are path-dependent. Since, in strong coupling, the path is ill-defined we can only hope to introduce alternative operational quantities and demand correspondence in the limit of weak coupling. This is done with the quantities adiabatic work, operational heat, and ergotropy which characterise the energy change during a general quantum process in an operational fashion. In a second step, a relation is drawn to a recently established operational second law and criteria are given for the resulting notion of heat to be positive or negative in a specific process.

We conclude in Chapter 5 and give an outlook on potential future research within this quantum operational framework of thermodynamics. Some of the ideas presented in that chapter are in fact work-in-progress and form part of an ongoing endeavour for further development of this research area.

Notation and terminology

This thesis lies at the intersection of three different disciplines: thermodynamics and statistical mechanics, quantum physics, and information theory. Consequently, it is unavoidable that some notational inconsistencies will appear compared to convention

in the different disciplines. For instance, we use U to refer to unitary operators as is common in quantum physics rather than to the internal energy (which is instead denoted by E). H refers to (time-independent) Hamiltonian operators, while entropies are denoted by the letter S . While definitions in the thesis will be unambiguous we nonetheless provide a further notational guideline in order to minimise the potential for misunderstanding.

We use the Greek letters $\rho, \sigma, \pi, \tau, \omega$ for mixed states, and $|\psi\rangle$ and $|\phi\rangle$ for pure states. All states assumed to be normalised, i.e., $\text{tr}[\rho] = 1$. Since everything in this thesis is expressed in the Schrödinger picture, time-dependence is mostly omitted for states. For most other operators time-dependence is explicitly indicated. Moreover, in the case of Hamiltonians we write $K(t) = H + V(t)$ to explicitly distinguish between the time-dependent and the time-independent part. Operators are generally written without a caret. Physical constants like k_B and $\hbar$ are set to unity apart from a few places where they are explicitly mentioned. Throughout the thesis, inverse temperature rather than temperature is used to describe thermal equilibrium and will in some places be simply referred to as ‘temperature’. Hilbert spaces are assumed to be discrete and finite. Some further nomenclature follows.

Nomenclature

$\Rightarrow$	‘implies’
$\dot{A}(t)$	time-derivative $\frac{d}{dt}A(t)$
M^T	matrix transpose of M
$M^\dagger$	Hermitian conjugate of M
$T_{\leftarrow}$	time-ordering operator (T : process duration)
α	optimisation parameter [Equation (3.7)]
β	inverse temperature $(k_B T)^{-1}$; here, contrary to conventional terminology mostly referred to as ‘temperature’
$\delta_{n,m}$	Kronecker delta
$\delta W, \delta Q$	pseudo-differentials of work W and heat Q
ϵ_j and κ_0	eigenvalues of Hamiltonians
ϵ_{lmn}	Levi-Civita symbol
σ_j	with index $j \in \{x, y, z\}$: Pauli matrices
E	internal energy
$\hbar$	reduced Planck constant; here: $\hbar = 1$ (apart from Box 3.1 and Appendix B)
$\mathbf{I}$	identity operator
k_B	Boltzmann constant
U	unitary (evolution) operator
$\mathcal{W}$	ergotropy [Equation (2.14)]

Abbreviations

CPTP	completely-positive and trace-preserving
LEMBAS	local effective measurement basis
LOCC	local operations and classical communication
ML	Margolus-Levitin
MT	Mandelstam-Tamm
QSL	quantum speed limit

A note on language

It will not escape the reader that this thesis is written in first person plural. The author would like to reassure the reader at this point that the use of the plural is neither owed to schizophrenic tendencies nor an inflated ego but much rather intended to be in accordance with what seems to be common practice in physics. This culture of writing in the plural has the positive effect of falling in line with the understanding that the practice of scientific advancement may always be seen as a dialogue (or indeed a multilogue) amongst those who dedicate their efforts and enthusiasm to it. In this spirit the reader should very much feel invited to see herself as an active participant in the thoughts which are to be developed and presented in this thesis.

Nonetheless, while the results which have previously been published and are presented here were developed collaboratively, this thesis is the author's own work entirely. Consequently, any conceptual and representational errors in the following chapters are the author's full individual responsibility.

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Introduction: (Quantum) Thermodynamics

“[Thermodynamik] ist die einzige physikalische Theorie allgemeinen Inhaltes, von der ich überzeugt bin, dass sie im Rahmen der Anwendbarkeit ihrer Grundbegriffe niemals umgestossen werden wird [...]”¹

Albert Einstein

“[...] everything appears to indicate that out of the classical theory the great principles of thermodynamics will not only maintain intact their central position in the quantum theory but will perhaps even extend their influence.”²

Max Planck

This chapter provides an introduction to the main concepts of thermodynamics.

First, it introduces the laws of thermodynamics and discusses the relationship with statistical mechanics.

¹“[Thermodynamics] is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown [...]” [Schilpp, 1969]

²[Planck, 1922]

In the second section, Jaynes' maximum entropy principle provides a justification for the Boltzmann-Gibbs distribution. Having established this notion of thermal equilibrium, we then re-examine the first and second law from a quantum information theoretic perspective.

The last section of the chapter focusses on the limitations and boundaries of conventional, equilibrium thermodynamics and raises questions relevant for the extension to finite-size and finite-time regimes.

This chapter hence serves as an introduction to (quantum) thermodynamics and the operational character of the present approach to be developed further in the following chapters.

1.1 Thermodynamics and its laws

The discipline of thermodynamics owes its birth to the industrial revolution which brought about fundamental changes to the conception of human labour [Marx, 1867]. The driving force behind these paradigmatic shifts were increased mechanisation and, in particular, the development of heat engines which sparked and fuelled the study of work, heat, and efficiency.

Since its initial establishment by Carnot [1824] in the early 19th century, through to its foundation on statistical mechanics at the turn of the century [Gibbs, 1902], and into the information age and the 21st century, thermodynamics has proved a robust and reliable theory. It not only survived the relativity and quantum revolutions that re-defined physics from its core in the first half of the 20th century, but crucially influenced the discovery and early development of the latter [Planck, 1900, 1922, 1943]. At the time of its pragmatic inception, thermodynamics was predominantly applied to the study of mechanical devices and systems whose constituent parts are well described by Newtonian mechanics. Today, it is successfully used to explain

phenomena along the whole range of modern physics from small quantum systems like cold atoms experiments to phenomena like black holes deep in the relativistic regime. It can hardly be overstated quite how remarkable the theory’s breadth of applicability and robustness have turned out to be in the face of profound paradigmatic shifts. Despite its long history and the fundamental nature of its basic statements, thermodynamics remains a vibrant field of research that has since its inception continuously yielded new and groundbreaking results. This holds true in current times, the 21st century, as much as ever. Most recent results are not based on an overturning of previous canon but have rather shown to be fruitful in extending the range of applicability of thermodynamics (and its younger sibling statistical mechanics). In this sense, thermodynamics continues to be a particularly constructive research field. Its much-debated second law serves as a particularly illustrative example: while no physicist will expect its basic statements to be drawn into question³, the law has seen a number of refinements and a new derivation rooted in fluctuation theorems [Jarzynski, 1997; Tasaki, 2000].

In relation to Albert Einstein’s quote at the beginning of this chapter, it is worth pointing out that thermodynamics, not least due to its foundation in statistical mechanics (cf. Section 1.1.1), is unique amongst the main theories of physics in that the ‘framework of applicability of its basic concepts’ is well defined within the theory itself (or within its grounding in statistical mechanics). One of the aims of the emerging field of *quantum thermodynamics* is to expand this framework and to increase its range of applicability. In addition, quantum thermodynamics may also offer a new perspective on existing notions of thermodynamics [Partovi, 1989], in a similar fashion to what we present in this chapter.

³It has been argued (e.g. by Čápek and Sheehan [2005]) that it is the lack of precision inherent to the second law which lends it its universality. In fact, different formulations apply in rather different contexts and under different assumptions rendering some of them incomparable.

This thesis falls within this line of research: the ambition to extend the range of applicability of thermodynamics rather than trying to overturn previous results. Before we highlight the limitations of conventional, textbook thermodynamics we briefly paraphrase its fundamental laws in Box 1.1. Recognising the theory’s shortcomings and restrictions will open the door towards further extending it into the quantum realm based on an operational approach (What is meant by *operational* here will be explained at the end of this chapter).

Box 1.1: The laws of thermodynamics

0 Thermal equilibrium states exist. Two systems independently in equilibrium with a third are also in equilibrium with each other.

I Energy is globally conserved and its changes come in two forms: work and heat.

$$\Delta E = W + Q. \quad (1.1)$$

II No work can be extracted from a closed equilibrium system during a cyclic variation of a parameter by an external source.

III A homogenous system at zero absolute temperature has no entropy. This limit is impossible to reach within finite time by thermodynamic means.

Notoriously, the laws of thermodynamics (in particular the second one) can be expressed in a number of different ways, some of which seem unrelated at first sight⁴. In textbooks, it depends on the predominant viewpoint which formulation of each law is preferred⁵. The statements presented in Box 1.1 are standard enough that further discussion of their historic attribution may be omitted. We only mention that the

⁴Cápek and Sheehan [2005], for instance, list 21 different formulations of the second law.

⁵There is no shortage of modern thermodynamics textbooks aimed at various levels of reader expertise. The excellent treatments by Callen [1985]; Balian [1991a]; Blundell and Blundell [2006]; Fließbach [2010]; Kondepudi and Prigogine [2015] may serve as examples of the vast canon. This brief introduction is closest in spirit to the unorthodox, and fully quantum viewpoint adopted by Balian [1991a,b], and the similar approach by Gemmer et al. [2009] and Mahler [2014].

formulations given here are commonly attributed to Fowler, Clausius, Thomson⁶, and Nernst. We have stated the laws in simplistic form at the cost of remaining somewhat vague. A more substantive discussion will follow in Section 1.2.

To a scientist it is appealing to formulate a theory on as few assumptions as possible. This ambition is certainly common in thermodynamics where it is debated how many laws or basic postulates are necessary for the theory⁷. The arguably most popular thermodynamics textbook in the English-speaking world [Callen, 1985] makes no explicit mention of the conventional laws at all but rather highlights the role of the concept of entropy and bases the theory on an alternative set of postulates.

Moreover, it is possible to derive thermodynamics from underlying microscopic considerations using statistical mechanics. In this sense the nature of the laws may lose its fundamental character anyway⁸. Consequently, we now briefly consider the relationship between thermodynamics and statistical mechanics. This will allow us to switch from a phenomenological viewpoint to a statistical mechanical one in Section 1.2 where we elaborate on the nature of states and processes which are of relevance in thermodynamics.

⁶This formulation of the second law is based on statements by Lord Kelvin and conventionally referred to as ‘Thomson’s formulation of the second law’ [Allahverdyan and Nieuwenhuizen, 2002, 2005; Gemmer et al., 2009]. In this attribution, William Thomson is of course one and the same person as Lord Kelvin: he was awarded the lordship later in his life. His original statement of the second law is also commonly found in the literature and is usually referred to by his later name: *It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects* [Thomson, 1851]. Planck [1917] later reformulated this law by stating that *It is impossible to construct an engine which will work in a complete cycle, and produce no effect except the raising of a weight and the cooling of a heat-reservoir* in what is often termed the ‘Kelvin-Planck’ statement of the second law. We here prefer the formulation by Allahverdyan and Nieuwenhuizen as it provides a clearer context for Chapter 4.

⁷For instance, we might have included the *minus first law* in Box 1.1. Simply put, it states that physical systems tend towards thermal equilibrium when left to themselves. We have omitted the law in this section since it has not found its way into the conventional canon. It is, however, discussed in Section 1.2.3 where we contrast it to the second law.

⁸Nonetheless, here and in the rest of this thesis we keep in mind Anderson’s famous dictum that *‘More is different’* [1972]. It is far from evident that all macroscopic thermodynamic effects would be explicable by reduction to microscopic considerations.

1.1.1 Thermodynamics and statistical mechanics

Thermodynamics, much like electrodynamics and mechanics, is a macroscopic theory in the sense that the basic variables that enter the description are of a macroscopic nature. Nonetheless, it is possible to derive thermodynamics from an underlying microscopic theory like Newtonian or quantum mechanics. Such a derivation is enabled by the vehicle of statistical mechanics whose structural approach was pioneered by Gibbs [1902] and is a standard part of undergraduate syllabi today (e.g. [Fließbach, 2010]). It has been extended by explicitly quantum physical derivations in the last decades [Balian, 1991a; Gemmer et al., 2009].

In order to relate the microscopic to the macroscopic view we need to be clear about what the basic elements of the microscopic description are. In the context of classical thermodynamics, a microstate is a state which is fully characterised by the system's microscopic variables, for instance, the positions and momenta of all particles that make up the system – in other words: a point in phase space. Such a state is accessible if it is consistent with existing knowledge about the macrostate of the system and external constraints (for instance a fixed volume, a known number of particles, etc). In quantum physics, microstates may directly be associated with pure states of a quantum system.

Incorporating this notion of microstates, statistical mechanics rests on the pillar provided by its fundamental postulate which states that

A closed system in equilibrium has equal probability of being in each of its accessible microstates.

This statement forms the basis of Gibbs' approach to statistical mechanics [1902] which he based on earlier works by Boltzmann and other early thermodynamicists. It allows for a full derivation of equilibrium thermodynamics.

The appearance of a notion of probability in the fundamental postulate already hints at a strong relationship to information theory. This link was further elaborated by a later generation of theorists, in particular Brillouin [1962] and Jaynes [1957a,b]. However, the connection between information theory and thermodynamics has not been without controversy. In particular the question of what is meant by *entropy* remains contentious. Various types of entropy will in fact be introduced in this chapter. Box 1.2 provides a brief overview of the three most important ones, leaving mathematical details for later.

More recently, a sophisticated programme has been developed which aims to ground conventional statistical mechanics on an underlying quantum physical description. In particular, there have been efforts of deriving the fundamental postulate cited above (or an equivalent statement) from a notion of *typicality*. Here, the essential argument explains the emergence of thermality with entanglement between subsystems of a larger isolated system. In spite of significant successes these approaches have not yet arrived at a complete derivation of *thermalisation* from typicality arguments. Here, we mostly ignore the intricacies of these results but rather start from the fundamental postulate and Jaynes' principle of maximal entropy. Readers interested in questions of equilibration and thermalisation are referred to a recent review paper on the foundations of statistical mechanics by Gogolin and Eisert [2015] and references therein.

In the first part of this chapter thermodynamics has been described from a phenomenological viewpoint and its laws were introduced in an axiomatic fashion. We now consider anew the laws of thermodynamics and analyse more closely which states and processes are of relevance for the study of conventional thermodynamics. In doing so we will adopt a microscopic statistical mechanics viewpoint.

Box 1.2: Entropy

In this thesis we distinguish three types of entropy:

- The incremental **Clausius entropy** is defined by Equation (1.23) as being proportional (with a factor β) to the incremental heat in a reversible process. It hence applies to **reversible processes**.
- The **Boltzmann entropy** is given by Equation (1.10). It is a statistical measure of the number of accessible microstates associated with a given macrostate. It equals the **Gibbs entropy** which is a state function of macrovariables such as energy, volume, and particle number. Both entropies are called **statistical entropy** and it is this entropy which conventionally appears in Equation (1.21) (We point this out because below, Equation (1.21) is derived for the von Neumann entropy which equals the statistical entropy for thermal states). The statistical entropy applies to **equilibrium states** characterised by fixed macrovariables (cf. Box 1.3).
- There exists a large variety of **information theoretic entropies**. Here, we explicitly use the **von Neumann entropy** (Equation (1.3)) which is the standard entropy of quantum mechanics, and the related **Shannon entropy**. They apply to **quantum states** and to **probability distributions** (i.e., populations in a density matrix), respectively.

The von Neumann entropy allows for the definition of the **relative entropy** (called **Kullback-Leibler divergence** in the case of probability distributions) which is defined by Equation (1.6).

In order to differentiate them from the information theoretic entropies we refer to both the Clausius and the statistical entropy as **thermodynamic entropy**.

We will not distinguish the different entropies notationally and use the letter S for all of them.

1.2 Systems, states, and processes in thermodynamics

In this section we take a closer look at the categorisation of thermodynamic systems, the states which describe equilibrium, and the constraints which apply to thermodynamic processes. This discussion is of particular relevance considering that this thesis lies at the intersection of two fields – quantum physics and thermodynamics – with different terminologies. The secondary purpose of this section is thus to clarify specifically some of the terminology that will be used in later chapters.

1.2.1 Systems

In the context of thermodynamics, we may define a quantum system as a tuple of a quantum state and a Hamiltonian (ρ, H) . In the following we differentiate between *isolated*, *closed*, and *open* systems. We adopt the common terminology of referring to those systems as *isolated* whose evolution is governed by a time-independent Hamiltonian H . If a time-dependent Hamiltonian drives the system evolution we may split it up into a time-independent part H and a time-dependent part $V(t)$ ⁹:

$$K(t) = H + V(t). \tag{1.2}$$

The evolution of the system under such driving is unitary and we hence call the system *closed* or *unitarily driven*. All other systems are referred to as *open*. More specifically, we will later permit for processes that allow for a description in terms of CPTP maps (i.e., $\rho \rightarrow \rho' := \mathcal{M}(\rho)$ and $H \rightarrow H'$). In these cases it is possible for the system to become correlated with an external ancilla system, environment or a heat bath.

⁹In order to express dependence on some external control mechanism we could formally express $V(\mathbf{X})$ in terms of a set of control parameters $\mathbf{X} := \{X_j\}$ which may in turn be time-dependent.

We point out that one may adopt a viewpoint which considers unitary evolution of pure states with a time-independent Hamiltonian as the most fundamental quantum process¹⁰. All other processes are then considered as *effective* descriptions of the dynamics of a given subsystem while the whole system – the *universe* – remains isolated. It is this perspective which inspired aforementioned typicality considerations as well as the local effective measurement basis (LEMBAS) approach to thermodynamic processes which will be introduced in Box 2.6.

1.2.2 States

We have discussed the difference between micro- and macrostates both for classical and quantum systems in Section 1.1.1. There, we noted that in thermodynamics (macro-)states are described in terms of macroscopic variables such as volume V , the particle-number N , temperature T , and pressure P . A quantum state, on the other hand, is simply specified by its density matrix ρ .

In this section we introduce those states which are relevant for macroscopic thermodynamics before discussing thermodynamic processes in the following section. The discussion relates back to the laws of thermodynamics.

The nature of thermal equilibrium (0th law)

The zeroth law asserts that there is such a concept as thermal equilibrium and that it is characterised by a temperature parameter. Moreover, if two systems are separately in equilibrium with a third one, their temperatures are the same. The existence of thermometers and thermostats (i.e., heat baths at constant temperature) is a consequence of this law.

¹⁰A part of this viewpoint is encapsulated in *Stinespring's dilation theorem* which asserts that any completely positive map between two Hilbert spaces can always be understood as an effective local description of unitary evolution on a larger Hilbert space. The application of this theorem is colloquially often referred to as ‘going to the church of the larger Hilbert space’.

However, the zeroth law, being of a macroscopic nature, does not specify the microscopic description of thermal equilibrium. There are in fact several different but complementary perspectives commonly taken to derive the form of thermal equilibrium states. A derivation from microscopic principles, originally due to Pusz and Woronowicz [1978], and subsequently simplified by Lenard [1978], is given in Chapter 2. Alternatively, one may follow the historical, statistical approach by Boltzmann which was later formalised in terms of thermodynamic ensembles by Gibbs [1902]. The thermal distribution and the corresponding states are commonly named after these two founders of statistical mechanics. Thirdly, a derivation from a completely information theoretic perspective is due to Jaynes [1957a,b] and derives the same states by maximising the (information theoretic) entropy. Lastly, much recent and ongoing research is devoted to studying equilibration and, more strongly, thermalisation which naturally arises as a property of a subsystem of a larger quantum system under certain conditions [Gogolin and Eisert, 2015; Gemmer et al., 2009]. This latest line of research essentially aims to reduce the previous approaches, in particular the statistical mechanical one, to a more fundamental level. Using the aforementioned concept of *typicality*, there has been significant progress towards motivating statistical mechanics' fundamental principle of equal a priori probabilities as an effective consequence of dynamics and entanglement. We leave an overview of this foundational research to the existing literature [Gogolin and Eisert, 2015]. Here, we content ourselves with starting from an axiomatic maximum entropy standpoint rather than aiming to further reduce this approach to underlying principles. In this spirit, Box 1.3 introduces the *maximum entropy principle*.

Box 1.3: The maximum entropy principle

The maximum entropy principle goes back to two papers by Jaynes [1957a,b] which address the question:

Given the expectation values $\langle O_k \rangle$ of a set of observables O_k what equilibrium state τ should be assigned to the system?

Jaynes argues that one should assign that state to the system which has the least informational bias: the equilibrium state τ should be the one which maximises the information theoretic (von Neumann) entropy

$$S(\rho) := -\text{tr}[\rho \log \rho]. \quad (1.3)$$

In order to find τ , Langrange multipliers λ_k may be introduced and variation is performed over a trial state ρ (which equals τ at maximum entropy):

$$\Lambda(\rho) = S(\rho) - \sum_k \lambda_k \text{tr}[O_k \rho] - \lambda_0 \text{tr}[\rho]. \quad (1.4)$$

Here, the last term ensures normalisation of ρ . Under these conditions (i.e., $\langle O_k \rangle$ given and ρ normalised) the equilibrium state is found by varying $\Lambda(\rho)$ with respect to a real parametrisation of the density operator ρ , taking into account that all involved operators are Hermitian. In general, the resulting equilibrium state τ is given by

$$\tau = \frac{1}{Z} \exp[-\sum_k \lambda_k O_k], \quad (1.5)$$

where the *partition sum* $Z := \exp[\lambda_0 + 1] = \exp[-\sum_k \lambda_k O_k]$ ensures normalisation.

Without actually performing the variation of Equation (1.4) we may show that Equation (1.5) indeed maximises the von Neumann entropy S by first introdu-

cing the relative entropy [Vedral, 2002]

$$R(\rho||\sigma) := \text{tr}[\rho \log \rho] - \text{tr}[\rho \log \sigma], \quad (1.6)$$

and then using this relationship to express the entropy difference between two arbitrary states ρ and σ as

$$\Delta S = S(\sigma) - S(\rho) = \text{tr}[(\rho - \sigma) \log \sigma] + R(\rho||\sigma). \quad (1.7)$$

Substituting $\sigma \rightarrow \tau$ from Equation (1.5) we obtain:

$$\Delta S = S(\tau) - S(\rho) = \sum_k \lambda_k (\text{tr}[\tau O_k] - \text{tr}[\rho O_k]) + R(\rho||\tau) \quad (1.8)$$

which, under the condition that the expectation values of O_k are fixed (i.e., the same for τ and ρ), is strictly larger than zero unless $\rho = \tau$ due to Klein's inequality [Klein, 1931; Nielsen and Chuang, 2000; Ruskai, 2002]. Hence, the von Neumann entropy of τ is larger than that of any other state ρ . In other words, τ is the maximum entropy state which complies with given expectation values $\langle O_k \rangle$.

Thermal equilibrium states as given by Equation (1.5) are rather general in nature. By considering the more specific settings related to the *thermodynamic ensembles* (introduced in Box 1.4) we may express the principle of equal a priori probabilities as well as the more specific expression of canonical equilibrium states which will be of relevance for the following chapters.

Box 1.4: Ensembles in statistical mechanics

The study of statistical mechanics can be done in different ensembles which correspond to different experimental conditions. Three ensembles in particular are of practical importance

- In the **microcanonical ensemble** the internal energy E of the system is fixed up to some small value ΔE .

This corresponds to an isolated system which can neither exchange energy, nor particles with its surroundings. The equal a priori probability principle arises in this context.

- In the **canonical ensemble** only the average energy $\langle H \rangle$ is fixed.

This condition entails the assignment $O_k = H\delta_{1,k}$ in Equation (1.4). The canonical ensemble corresponds to an experimental setting where the system under study may exchange heat with its surroundings at a constant inverse temperature β (i.e., the system is coupled to a single heat bath).

- The **macrocanonical ensemble** describes a situation where particle exchange between the system and its surroundings is permitted.

In this case the average number of particles and the average energy are fixed, formally expressed as $O_k = H\delta_{1,k} + N\delta_{2,k}$ in Equation (1.4).

Re-expressing Equation (1.5) for the microcanonical ensemble we write the corresponding equilibrium state as

$$\tau_\mu = \frac{1}{d_E} \mathbf{I}_E + \mathcal{O}(\Delta E), \quad (1.9)$$

where $\mathbf{I}_E$ is the identity operator on the d_E -dimensional subspace corresponding to energies between E and $E + \Delta E$. In the limit $\Delta E \rightarrow 0$ Equation (1.9) is a statement

of the principle of equal a priori probabilities. In this case both the von Neumann and the Shannon entropy reduce to the Boltzmann entropy¹¹

$$S(\tau_\mu) = \log d_E. \quad (1.10)$$

Turning the attention to the canonical ensemble, the notorious form of the thermal state may directly be recovered from Equation (1.5) by keeping a fixed average of the internal energy $\langle H \rangle$, and state normalisation as the only two constraints:

$$\tau_\beta := \frac{1}{Z} e^{-\beta H}. \quad (1.11)$$

Here, the inverse, absolute temperature¹² β has been introduced as a Lagrange multiplier (i.e., $\beta = \lambda_1$ in Equation (1.4) with $O_1 = H$). It is in fact the same as the relative temperature which appears in the zeroth law [Balian, 1991a].

It should be noted that the information theoretic approach underlying the derivation in Box 1.3, while certainly appealing to intuition, is not without criticism. In particular, an extension to out-of-equilibrium scenarios is hindered by the reliance on the von Neumann entropy which is not universally considered as being thermodynamically appropriate outside the equilibrium regime.

At any rate, the maximum entropy approach outlined in Box 1.3 provides a clear derivation of equilibrium states for equilibrium thermodynamics. It follows the same spirit as Gibbs' early treatment and the principle of equal probabilities. An alternative derivation along with a generalisation of the notion of equilibrium is provided in the

¹¹As before we allow ourselves to relax explicit unit notation: without loss of generality we have set the Boltzmann constant to unity ($k_B = 1$) and have also not specified the base to which the logarithm should be taken. Re-labelling $k \equiv k_B$ and $W \equiv d_E$ Equation (1.10) may be expressed as $S = k \log W$ to match the famous inscription on Ludwig Boltzmann's tombstone in Vienna.

¹²In this thesis we prefer the use of the inverse temperature $\beta = (k_B T)^{-1}$ (where k_B is the Boltzmann constant) over the absolute temperature T . Contrary to conventional terminology, we occasionally refer to β rather than T as 'temperature'. Since temperature only appears as a parameter characterising the thermal (canonical equilibrium, Boltzmann-Gibbs) distribution this poses no issue.

first section of Chapter 2. First, however, we characterise the processes that are considered in equilibrium thermodynamics in the following section by introducing and discussing statements of the first and second law in quantum language.

1.2.3 Processes

In thermodynamics, processes are often characterised by which macroscopic variables remain unchanged. Depending on what quantity remains constant, thermodynamic processes are referred to as *isothermal* (constant temperature), *isochoric* (volume), *isentropic* (entropy), *isobaric* (pressure), etc¹³. A reversible process which does not allow for an exchange of heat between the system and external reservoirs is called *adiabatic*. This term can lead to some confusion as it is defined differently in quantum physics where *adiabatic* processes are those unitary processes which keep a diagonal state diagonal in the instantaneous eigenbasis of a time-dependent driving Hamiltonian. According to the adiabatic theorem the conditions for a process to be adiabatic are fulfilled if it happens slowly on a time-scale determined by the inverse of the smallest relevant energy gap of the driving Hamiltonian. In this sense quantum-adiabaticity bears similarity to the *quasi-static* regime in thermodynamics where it is asserted that due to slow evolution the thermodynamic system remains in equilibrium at each instant in time. The notion of adiabaticity will be of relevance in Chapter 4.

In general, all thermodynamic processes are governed by the first and second law. We here state them in quantum language.

Work and heat (1st law)

In conventional thermodynamics the first law establishes two separate forms of energy: work and heat. The distinction between them is made at a macroscopic level and carries an operational flavour. Within the clear confines of equilibrium thermodynamics

¹³Formally, appropriate reservoirs can be introduced as ancillary systems which keep certain macrovariables constant.

this distinction does not leave much room for ambiguity of what is work and what is heat. The situation looks rather different, however, once non-equilibrium processes and finite-size systems are considered. In Chapter 2, a variety of work extraction scenarios will be introduced and we will notice that not all corresponding notions of work are directly comparable to each other. For now, however, we may proceed to show how an infinitesimal form of the first law which is valid for quasi-static processes may be obtained from a quantum perspective.

We start by recognising the expectation value of the Hamiltonian as internal energy¹⁴

$$E := \text{tr}[\rho K(t)]. \quad (1.12)$$

For a quantum system the first law can be expressed by taking the differential of the internal energy:

$$dE = \text{tr}[K(t)d\rho] + \text{tr}[\rho dK(t)]. \quad (1.13)$$

This suggests defining of work and heat as

$$\delta W := \text{tr}[\rho dK(t)], \quad (1.14)$$

$$\delta Q := \text{tr}[K(t)d\rho]. \quad (1.15)$$

Assigning work and heat in this manner is popular because it fits physical intuition: changes in the system's energy ($dK(t)$) are associated with work while changes to the configuration of the system ($d\rho$) – its probability of being in a certain micro-state – are understood as heat¹⁵. For unitary evolution heat vanishes by virtue of the Liouville-von Neumann equation: $\dot{\rho}(t) = i[K(t), \rho]$. Equations (1.14) and (1.15) may be integrated to yield the total work and heat expended in a process. We denote

¹⁴The implications of this assignment, in particular with a view to the role of coherences in the energy eigenbasis, will be discussed in the following chapters.

¹⁵Based on this intuition, an extension to open systems is possible by identifying the relevant generators in a master equation as further infinitesimal heat contributions [Alicki, 1979].

these total quantities of work and heat as W and Q , respectively. The internal energy change will be referred to as ΔE .

Here, Equations (1.14) and (1.15) were introduced *ad hoc* in a phenomenological fashion. In general, it is not guaranteed that ρ and, moreover, $K(t)$ exist. In strong coupling, for instance, the identification of what is meant by $K(t)$ is not a priori obvious. For the purposes of this introductory chapter we assume that the heat in Equation (1.15) is exchanged with a (weakly-coupled) heat bath and the work in Equation (1.14) is exchanged with a (semi-classical) work source¹⁶. A more thorough treatment follows in Chapter 2, in particular in Box 2.6.

Furthermore, it is crucial to recognise that both work and heat are generally path-dependent quantities. It is for this reason that we have written δW and δQ rather than dW and dQ . As illustration we may consider the heat expended when pushing a piston into a cylinder filled with gas: it depends not only on the initial and final positions of the piston but also on how fast the piston is pushed. As a consequence of path dependence, in general, work and heat are not observables in the quantum mechanical sense if fluctuations are to be represented self-consistently [Talkner et al., 2007; Allahverdyan, 2014].

In order to establish correspondence to conventional equilibrium thermodynamics for Equation (1.13) we explicitly express the Hamiltonian $K(\mathbf{X}(t))$ in terms of a set $\mathbf{X}(t) := \{X_j(t)\}$ of time-dependent driving parameters $X_j(t)$. Inserting this into Equation (1.14) we have

$$\delta W = \sum_j \text{tr} \left[\rho \frac{\partial K(\mathbf{X})}{\partial X_j} dX_j \right]. \quad (1.16)$$

¹⁶This latter point will be further discussed around Equation (1.17).

This helps to highlight the relationship to the classical case where the incremental work

$$\delta W = \sum_j \Phi_j dX_j \quad (1.17)$$

is expressed in terms of generalised forces Φ_j for each displacement dX_j in parameter space. For instance, X_1 might be the system's volume and ϕ_1 , correspondingly, the pressure. Correspondence between Equations (1.16) and (1.17) is established with the identification of

$$\Phi_j := \text{tr} \left[\frac{\partial}{\partial X_j} K(\mathbf{X}) \right] \quad (1.18)$$

as generalised forces. Here, we have implicitly made a semi-classical approximation by assuming that the X_j are in fact parameters rather than quantum operators describing the interaction between work source and system. This assumption is justified if fluctuations (and correlations) in the X_j are negligible [Balian, 1991a].

Having established a relationship between our microscopic description and the common macroscopic expression of work we may now consider Equation (1.15) again in order to relate it to the conventional expression for heat in a similar fashion. Choosing ρ to be the canonical equilibrium state τ_β , the heat term can in fact be expressed in terms of the von Neumann entropy. This may be seen by taking the differential of the von Neumann entropy¹⁷

$$dS(\rho) = -\text{tr}[d\rho \log \rho], \quad (1.19)$$

and then applying it to a thermal state¹⁸ $\tau_\beta = Z^{-1} \exp[-\beta K(t)]$:

$$dS(\tau_\beta) = \beta \text{tr}[d\tau_\beta K(t)] = \beta \delta Q. \quad (1.20)$$

¹⁷Note that $\text{tr}[\rho d(\log \rho)] = 0$.

¹⁸There is a subtlety here in that we want to insert an instantaneous canonical state corresponding to the Hamiltonian $K(t)$ at time t (Z in the above expression is thus also time dependent). Equations (1.20) and (1.21) as well as derived equations in the following section are restricted to quasi-static, reversible processes for this reason.

Consequently, Equation (1.13) may be re-written as

$$dE = \delta Q + \delta W = \beta^{-1}dS + \sum_j \Phi_j dX_j. \quad (1.21)$$

This is in fact the fundamental statement of the first law as it may be found in a textbook¹⁹ [Gibbs, 1902].

Extracting work (2nd law)

While a simple yet general derivation of the second law from a microscopic description remains elusive [Gemmer et al., 2009], we may gain an intuition for the quasi-static case by noticing that Equation (1.20) is in fact a statement of the Clausius equality. Moreover, intuition is further aided by considering Equation (1.8) again for the canonical ensemble (i.e., Equation (1.11)), to wit:

$$\Delta S = S(\tau_\beta) - S(\rho) = \beta \text{tr}[(\tau_\beta - \rho)H] + R(\rho||\tau_\beta). \quad (1.8')$$

Then, with the identification $\text{tr}[(\tau_\beta - \rho)H] = Q$, in the spirit of Equation (1.15), Equation (1.8') becomes

$$\Delta S = \beta Q + R(\rho||\tau_\beta) \geq \beta Q. \quad (1.22)$$

Here, the last relation follows again from Klein's inequality²⁰. We emphasise that Q can be negative: a cooling process may consequently reduce a system's entropy.

¹⁹In the literature a third term, $\sum_j \mu_j dN_j$, usually appears. It expresses the energy change due to exchange of particles belonging to species j (μ_j is the corresponding chemical potential, N_j the corresponding particle number). In the canonical ensemble we note that this sum may formally be absorbed into the second term of Equation (1.21) with the chemical potentials playing the role of generalised forces.

²⁰Interestingly, one may in the same way establish an upper bound to the entropy change as well:

$$\Delta S = S(\tau_\beta) - S(\rho) = \text{tr}[(\rho - \tau_\beta) \log \rho] - R(\tau_\beta||\rho) \leq \text{tr}[(\rho - \tau_\beta) \log \rho].$$

We have hence obtained a version of the Clausius statement of the second law: Equation (1.22) may be interpreted as a second law for discrete thermalisation processes (i.e., at constant Hamiltonian H). A more rigorous treatment by Anders and Giovannetti [2013] reveals that this interpretation is indeed appropriate and extends to more general processes. A similar derivation has also been presented by Sagawa [2012] in a wider context.

Taking the infinitesimal limit, this version of the second law states that the entropy increment associated with a state transformation is lower bounded by the infinitesimal heat weighted by β :

$$dS \geq \beta \delta Q. \quad (1.23)$$

Equality is attained for quasi-static processes (i.e., processes for which at each point in time the system state remains arbitrarily close to thermality) as in Equation (1.20). As mentioned in Box 1.2, under the restriction to quasi-static processes, Equation (1.23) may in fact be invoked as a definition of either the Clausius entropy or of the inverse absolute temperature β .

It is worth pointing out that we have used the same mathematical identity in two apparently different physical contexts: first, in Box 1.3, we used Klein’s inequality to argue that the (Boltzmann-) Gibbs state should be considered as equilibrium state. In the second case, we applied the same inequality when deriving the second law²¹. In this latter context, ΔS was not interpreted as an abstract mathematical quantity to be minimised but rather as the entropy change in an actual thermodynamic process.

In relation to these two different applications of Klein’s inequality, a subtle but important point which we have so far glossed over merits clarification: it has been ac-

²¹On a historical side-note, one may appreciate that Klein [1931] derived his inequality with the aim to study the second law from a quantum perspective. He used it to prove that the Shannon entropy, which was known under a different name at the time, is minimal in the diagonal basis and hence generally decreases for a unitary process that starts in a diagonal state (unless the process is adiabatic). He then showed, for the case of bi-partite systems, that the von Neumann entropy is generally sub-additive and exactly additive only for separable states.

knowledged [Brown and Uffink, 2001; Campisi and Hänggi, 2011], albeit not widely, that the second law does not include the evolution of an autonomous (i.e., mechanically isolated) system from a non-equilibrium state towards equilibrium. The occurrence of such evolution is in fact a separate ingredient of thermodynamics and is referred to as either *Equilibrium Principle* or *Minus First Law*. The difference between the minus first and the second law is reflected in the structure of this chapter where Section 1.2.2 (States) is concerned with the character of thermodynamic equilibrium. We have here, as pointed out above, left the question of equilibration (and, more strictly, thermalisation) aside and introduced the notion of equilibrium from an information theoretic viewpoint. The present section on processes, on the other hand, includes the introduction of the second law proper. As noted in the previous paragraph, the same distinction is inherent to Equations (1.22) and (1.8'), on the one hand, and Equations (1.20) and (1.23), on the other. In the first case an out-of-equilibrium state was compared to an equilibrium state (with a fixed Hamiltonian H), while in the second case we implicitly thought of quasi-static processes connecting equilibrium states (with respect to the instantaneous Hamiltonian $K(t)$). This was also highlighted in footnote 18.

Considering Clausius' expression (Equation (1.23)) once again, a bound on the extractable work in a reversible process may be derived by inserting the first law into the second law (i.e., inserting δQ from Equation (1.21) into Equation (1.23)):

$$\delta W \geq dE - \beta^{-1}dS =: dF, \quad (1.24)$$

where we have identified the right-hand side of the inequality as the incremental free energy. This inequality implies that an amount of work greater or equal to the free energy change has to be invested to change the system from one state to another. If the free energy change is negative its absolute value puts an upper limit on the

extractable work (which is given by $-W$). In Chapter 2 we will return to the notion of free energy when studying work extraction in Section 2.3.

This concludes our brief overview of macroscopic thermodynamics. We now delineate its boundaries before continuing with a more general discussion of work extraction in the finite-size quantum regime in the following chapter.

1.3 Quantum thermodynamics?

Thermodynamics in its conventional form is limited in four (overlapping) ways:

- I) In its textbook form, we may also refer to thermodynamics as *thermostatistics* since it is (mostly) restricted to equilibrium states and quasi-static processes. This restriction has been addressed since the beginning of thermodynamics and is known as the field of *non-equilibrium thermodynamics*. It is by now an advanced area of study in its own right [de Groot and Mazur, 1984]. It does however still share the following three further limitations.
- II) Thermodynamics, in its equilibrium and non-equilibrium version, is understood as a macroscopic theory. It applies, if not to systems of infinite size (i.e., in the thermodynamic limit), to systems that are at least large enough for fluctuations to become irrelevant such that the grounding of thermodynamics in statistical mechanics becomes justifiable. From the point of view of statistical mechanics these fluctuation relations have developed into a research field of their own and have, in particular due to advances in the last couple of decades [Jarzynski, 1997; Crooks, 1999; Tasaki, 2000], kindled a growing scientific interest²².
- III) The ‘quantumness’ of thermodynamic media is not understood as in itself posing an obstacle for thermodynamics: the application of equilibrium thermodynamics

²²See [Esposito et al., 2009; Campisi et al., 2011] and references therein.

to quantum media has been ubiquitous in standard textbooks for decades. Nonetheless, results about the thermodynamic role of quantum phenomena such as coherence and entanglement, in particular in finite-size systems, remain patchy and a unified understanding is still lacking at this stage.

IV) Another, perhaps less emphasised limitation of conventional thermodynamics is that it is usually not concerned with the time-scales of processes: the focus rather lies on the (statistical) possibility²³ of a given process to occur but not on its duration.

These limitations are widely acknowledged and pose no fundamental issue by themselves as long as thermodynamics results are not applied outside their range of validity. Additionally, as pointed out, they have all been addressed and have sparked dedicated research. We highlight them here because the field of *quantum thermodynamics*, while lacking a canonical definition, tends to not impose these restrictions a priori. It is hence, in a broader way, well posed to address the questions:

Are there quantum effects that lead to a genuine thermodynamic advantage or disadvantage?

And conversely: are there thermodynamic effects whose nature is genuinely quantum?

In addressing aspects of these questions it is worth recognising that two complementary mindsets have been inherent to the study of thermodynamics since its

²³The grounding of thermodynamics in statistical mechanics is relevant to the terminology here: for a process to be thermodynamically ‘impossible’, does not mean that it is microscopically inconceivable but rather, loosely speaking, *highly unlikely*. If we consider for instance, a box filled with a Newtonian point-particle gas, initially homogeneously distributed, we would not expect to find all particles located in just one half of the box at some point in time. Such a process, effectively reducing the entropy of the gas, is ‘impossible’ as a consequence of the second law. Nonetheless, it is absolutely ‘possible’ in the microscopic sense, just highly unlikely unless the number of particles is very small (probing an ideal gas of N particles at an arbitrary time, for instance, will, with probability 2^{-N} , detect all particles in one half of the box). This illustration highlights the statistical nature of the second law which is reflected in its statement in terms of entropy.

beginnings. One which we call the *constructive* mindset, takes the perspective of an engineer and places the agent at the forefront of the investigation. Studies of limitations to the efficiency of thermal engines are a paradigmatic example of what may be an interesting research question from this perspective. This mindset is more phenomenological. The other viewpoint, which we call the *deductive* mindset, aims to derive thermodynamic behaviour from underlying microscopic descriptions. A paradigmatic example of this perspective is the theoretic study of thermalisation, for instance starting with arguments of typicality [Gemmer et al., 2009]. If the constructive view was related to phenomenological thermodynamics the deductive perspective is closer to the mindset of statistical mechanics. It is clear that both perspectives are but viewpoints of the same topic. They are both concerned with the same phenomena, and (must) produce the same results. Furthermore, they are by no means exclusive.

However, an acknowledgement of these two different mindsets is useful in understanding different assumptions – what is considered ‘natural’ – when trying to answer a specific question. This is apparent, for instance, in the different approaches to deriving the Boltzmann-Gibbs distribution which describes thermal states. The derivation outlined in this chapter falls more within a deductive perspective (albeit inspired by an information theoretic mindset rather than a microscopic, physical one). The derivation of thermal equilibrium states in the following chapter is undertaken from a more constructive viewpoint. We will also encounter the distinction again when considering work extraction in Section 2.3 of the following chapter: from the deductive perspective, one usually starts with a large system governed by a time-independent Hamiltonian and then considers effective local dynamics of subsystems – for instance, in order to ascribe energy changes of a single subsystem to either work or heat. A local time-dependent dynamics is here seen as an effective reduction of some underlying larger system description. In the constructive approach, which will be taken

here with respect to work extraction, time-dependence of the system Hamiltonian is seen as ‘natural’ input into the problem, reflecting some external (arguably ‘semi-classical’) control of the system as would be encountered in a quantum technology laboratory.

This thesis adopts a mindset closer to the constructive viewpoint in an operational approach. It merits a clarification what is meant by *operational* in this context. After all, it has been recognised that thermodynamics in its conventional form is already of an operational nature [Mahler, 2014] as we have already highlighted, for instance, when discussing the first law and the difference between work and heat. The theory’s formulation in terms of specific thermodynamic processes (quasi-static, isochoric, adiabatic, etc.) is contingent on the existence of an experimenter, an agent that can control or design a thermodynamic system, apparatus, or engine. Here, we want to emphasise a notion of operationality that takes inspiration from the field of quantum information theory where *quantum operations* describe possible state transformation from that point of view. In the following chapters we keep this perspective in mind and explicitly study the energetics of quantum operations in Chapter 4.

Passivity and unitary work extraction

This chapter sets the scene for the results presented in the following chapters by introducing the framework of unitary work extraction as well as the related concepts of ergotropy and passivity. We review a derivation of thermal states from microscopic principles and present some considerations about the role of quantum correlations in unitary work extraction. This is followed by an in-depth contextualisation of the framework of unitary work extraction compared to alternative approaches such as macroscopic equilibrium and non-equilibrium thermodynamics, fluctuation theorems, and single-shot thermodynamics including the resource theoretic framework of thermal operations, and finally the so-called local effective measurement basis (LEMBAS) principle. In relation to these approaches, we reconsider the concept of unitary work extraction and fully characterise it.

The previous chapter introduced thermodynamics from a quantum mechanical perspective. Specific focus was put on describing both states and processes that the theory applies to. In particular, we introduced the Boltzmann-Gibbs distribution that characterises thermal states by reference to Jaynes’ principle of maximal entropy. In an alternative approach, thermality may be introduced by finding those states from which no work can be extracted (in a cyclic, unitary process as described below) [Pusz and Woronowicz, 1978; Lenard, 1978]. This derivation carries an operational flavour in that it relates the property ‘equilibrium’ to the task of work extraction. We begin the chapter by introducing the notion of passivity.

2.1 Passive states

Passive states are defined as being those states from which no work can be extracted in a cyclic unitary process (cf. Box 2.1).

Box 2.1: Cyclic unitary processes

Starting at time $t = 0$, the system is unitarily driven by some Hamiltonian

$$K(t) = H + V(t) \quad (2.1)$$

for an evolution time T with the condition that for $t \leq 0$ and $t > T$, $V(t) = 0$.

Due to the von Neumann equation,

$$i \frac{d\rho(t)}{dt} = [K(t), \rho(t)], \quad (2.2)$$

any such driving gives rise to a unitary evolution operator $U(t)$ with the property that

$$\rho(t) = U(t)\rho(0)U^\dagger(t). \quad (2.3)$$

As a consequence of unitarity, any energy change of such a process must be considered work¹. Accordingly, the (average) work of a unitary process $\rho(0) \rightarrow \rho' := \rho(T)$ is given by

$$W = \text{tr}[\rho' H] - \text{tr}[\rho H] \quad (2.4)$$

From this expression one can obtain clear criteria under which a state is passive with respect to a given reference Hamiltonian H [Lenard, 1978; Allahverdyan et al., 2004; Skrzypczyk et al., 2015]. These are summed up in Box 2.2.

Box 2.2: Passive states

Given a state ρ and a reference Hamiltonian H , both written in their respective eigenbasis (increasing for H , decreasing for ρ),

$$H := \sum \epsilon_n |\epsilon_n\rangle\langle\epsilon_n|, \text{ with } \epsilon_{n+1} \geq \epsilon_n \forall n, \quad (2.5)$$

$$\rho := \sum r_n |r_n\rangle\langle r_n|, \text{ with } r_{n+1} \leq r_n \forall n, \quad (2.6)$$

ρ is passive with respect to H if and only if (1) ρ and H are diagonal^a in the same basis and (2) ρ contains no population inversion:

- 1) $[\rho, H] = 0$, and
- 2) $\epsilon_j < \epsilon_k \Rightarrow r_j \geq r_k$.

Below, where the reference Hamiltonian H is unambiguous we denote passive states by the letter π . Any state that is not passive will be called active^b.

^aA passive state π need not be diagonal in degenerate subspaces of H but the basis $\{|\epsilon_n\rangle\}$ may always be chosen such that it is (without loss of generality).

^bPopulation inversion in a laser medium is a familiar example of an active state.

¹Below we refer to such processes as *unitary work extraction* processes. In light of the fact that the energy change in any unitary process should always be considered work this terminology may seem tautological. At any rate, when we speak of ‘unitary work extraction’ here we think of work extraction scenarios where a time-dependent Hamiltonian $K(t)$ causes the system evolution. A work reservoir that absorbs the change in energy is tacitly implied. This understanding of work in quantum thermodynamics will be critically discussed in more detail in Section 2.3.

2.1.1 Activation, N-passivity, and complete passivity

When combining two or more identical passive states $\pi^{(k)}$ (each pertaining to a Hilbert space labelled by k), the resulting multi-partite state $\bigotimes_k \pi^{(k)}$ need not be passive. This process of system combination is hence called *activation*. The resulting combined state $\bigotimes_k \pi^{(k)}$ always commutes with the combined Hamiltonian $\sum_k H^{(k)}$ and thus fulfils criterion (1) of Box 2.2. Population inversion on the multi-partite system, however, is generally possible. Example 2.1 provides a minimalistic illustration of activation.

Example 2.1: Activation

In order to demonstrate activation with a simplistic example we consider a specific, passive qutrit state π . Its Hilbert space is spanned by some orthonormal basis $\{|1\rangle, |2\rangle, |3\rangle\}$. For a combination of two copies of π (i.e., $\rho_{tot} = \pi \otimes \pi$ and $H_{tot} = H \otimes \mathbf{I} + \mathbf{I} \otimes H$), we identify two levels of H_{tot} which show population inversion – hence demonstrating activation. We define

$$H = 2\epsilon |2\rangle\langle 2| + 3\epsilon |3\rangle\langle 3|, \text{ and} \quad (2.7)$$

$$\pi = \frac{1}{2} (|1\rangle\langle 1| + |2\rangle\langle 2|), \quad (2.8)$$

with $\epsilon > 0$. Denoting $|n, m\rangle \equiv |n\rangle \otimes |m\rangle$ it is easily seen that the combined state ρ_{tot} is active (with respect to H_{tot}):

$$\rho_{tot} = \frac{1}{4} (|1, 1\rangle\langle 1, 1| + |1, 2\rangle\langle 1, 2| + |2, 1\rangle\langle 2, 1| + |2, 2\rangle\langle 2, 2|) \quad (2.9)$$

In particular, the population of the energy eigenstate $|2, 2\rangle$ exceeds that of the unoccupied state $|1, 3\rangle$ even though the energy of the former is larger than that of the latter. Specifically, labelling the eigenvalues of H_{tot} as $E_{n,m}$ and the

corresponding populations $p_{n,m}$, we have

$$p_{2,2} = \frac{1}{4} > 0 = p_{1,3}, \text{ despite} \quad (2.10)$$

$$E_{2,2} = 4\epsilon > 3\epsilon = E_{1,3}. \quad (2.11)$$

This population inversion, which violates condition (2) in Box 2.2 for the total system, demonstrates activation in the state $\rho = \pi \otimes \pi$.

N-passivity

One may hence impose the additional requirement that the combination of a number N of identical passive systems as

- $\rho_N = \bigotimes_k^N \pi^{(k)}$, and
- $H_N = \sum_k^N H^{(k)}$,

still be passive². Here, k labels the N identical systems with reference Hamiltonians $H^{(k)} = H$. If ρ_N is passive with respect to H_N , π is called *N-passive*. We refer to states which are not *N-passive* as *N-active*.

In order to obtain a criterion for N-passivity, we consider condition (2) from Box 2.2 for ρ_N . Comparing two energy levels of H_N , $E_a = \sum a_j \epsilon_j$ and $E_b = \sum b_j \epsilon_j$ with $\sum a_j = \sum b_j = N$, condition (2) for passivity of ρ_N reads³:

$$\sum a_j \epsilon_j < \sum b_j \epsilon_j \Rightarrow \prod r_j^{a_j} \geq \prod r_j^{b_j}. \quad (2.12)$$

²Formally: $H_N = \sum_{k=1}^N H^{(k)} \otimes_{l \neq k} \mathbf{I}^{(l)}$

³Here and in the following we have $0^0 = 1$ while $0^n = 0$ for $n \in \mathbb{N}$. Furthermore, we define $\log(0) = -\infty$ for the sake of simplicity (and in spite of the inherent mathematical sloppiness in this assignment).

Since the logarithm is a monotonic function we may equally express the inequality on the right in terms of sums

$$\sum a_j \epsilon_j < \sum b_j \epsilon_j \Rightarrow \sum a_j \log r_j \geq \sum b_j \log r_j. \quad (2.13)$$

Complete passivity

If a state π is N -passive for all N (i.e., $N \rightarrow \infty$) it is called *completely passive*. A constructive proof that any completely passive state must either have Gibbs form, i.e., Equation (1.11), or be a ground state, has been given by Lenard [1978] based on an earlier paper by Pusz and Woronowicz [1978]. An alternative proof, which employs the concept of *virtual temperatures*, was recently published by Skrzypczyk et al. [2015]. In Appendix A, we provide a minimal proof based on the latter approach.

2.1.2 Remarks

We point out that the second step in the derivation of thermal states, i.e., going from passivity to complete passivity, crucially depends on the consideration of system composition. Gibbs states only emerge when a (possibly infinite) number of systems (or the other way around: subsystems) are taken into account. If, on the other hand, we are considering a physical system that is naturally constrained in size – for instance, the working medium of a heat engine – we may content ourselves with considering passivity a sufficient condition for equilibrium rather than the stricter restriction to thermality ($\hat{=}$ complete passivity) encountered in most studies. Even for a closed, finite-size system, coupling to thermal heat baths may in practice introduce thermality into the system. But, as for the system itself, this requirement only becomes natural in the limit of very large heat baths.

It is an obvious observation that the family of passive states is much richer both mathematically and physically than that of thermal states. Not being a single para-

meter family, its categorisation is more subtle. Taking two different thermal states for instance, we always know that the average energy will be larger for the one at higher temperature. When comparing two general passive states, on the other hand, one requires precise knowledge of the energy levels of H in addition to the states' populations in order to determine which one is more energetic: A generic comparison based on a single parameter like the temperature is not possible in general. This observation will be reconsidered in a more quantitative fashion in the following section (cf. Section 2.2.1).

2.2 Unitary work extraction and ergotropy

The results of the previous section provide an answer to the question

Which form do those states have from which no work can be extracted in a cyclic unitary process?

It refers us to passive states whose form is explained in Box 2.2. Based on Lenard's work [1978], Allahverdyan et al. [2004] investigated a follow-up question⁴:

What is the maximal amount of work that can be extracted from a system S by means of an external work source acting cyclically in a thermally isolated process?

In particular, the system S is to be described by a quantum state ρ and a (time-independent) reference Hamiltonian H . The process being *thermally isolated* is understood to imply that it is unitary. As noted before, for unitary evolution, any change in internal energy $\langle H \rangle$ must be work. For the following analysis we again express the reference Hamiltonian H in its *increasing* spectral decomposition, and

⁴See also [Bratteli and Robinson, 1997].

the state ρ in its *decreasing* eigen-decomposition; to wit (cf. Box 2.2):

$$H := \sum \epsilon_n |\epsilon_n\rangle\langle\epsilon_n|, \text{ with } \epsilon_{n+1} \geq \epsilon_n \ \forall n, \text{ and} \quad (2.5)$$

$$\rho := \sum r_n |r_n\rangle\langle r_n|, \text{ with } r_{n+1} \leq r_n \ \forall n. \quad (2.6)$$

The goal is now to transform ρ into that unitarily connected state which has the lowest internal energy, extracting the difference in internal energy in the process. After maximal cyclic, unitary work extraction, no further work can be extracted and the system ends up in a *passive* state π [Allahverdyan et al., 2004; Lenard, 1978; Pusz and Woronowicz, 1978]. This state π is unique up to degeneracies in the reference Hamiltonian H . Since a passive state's internal energy is fixed even in the presence of energetic degeneracies, they have no bearing on the arguments presented here and the reader may think of passive states as being unique with regard to a given Hamiltonian⁵.

The maximum work that can be extracted from a non-passive state ρ with respect to a reference Hamiltonian H via a cyclic unitary process ($\rho \rightarrow \pi = U\rho U^\dagger$) is given by the energy difference between ρ and that passive state π which has the same eigenspectrum:

$$\mathcal{W} := \text{tr}[(\rho - \pi)H] = \sum_{m,n} r_m \epsilon_n [|\langle\epsilon_n| r_m\rangle|^2 - \delta_{mn}]. \quad (2.14)$$

This quantity is called *ergotropy* [Allahverdyan et al., 2004] and it is always positive. It depends on the initial state ρ and the reference Hamiltonian H and we may write $\mathcal{W}(\rho, H)$, in order to explicitly state this dependence. Intuitively, ergotropy

⁵Some authors like to indicate the correspondence between the active state ρ and its passive state π by an index ρ . This notation is omitted in this thesis as there will not be any ambiguity as to which active states specific passive states correspond to. In addition, correspondence between states will be highlighted graphically in appropriate places.

encodes contributions to work extraction from both excitations and coherences. This is illustrated in Example 2.2 for the case of a qubit.

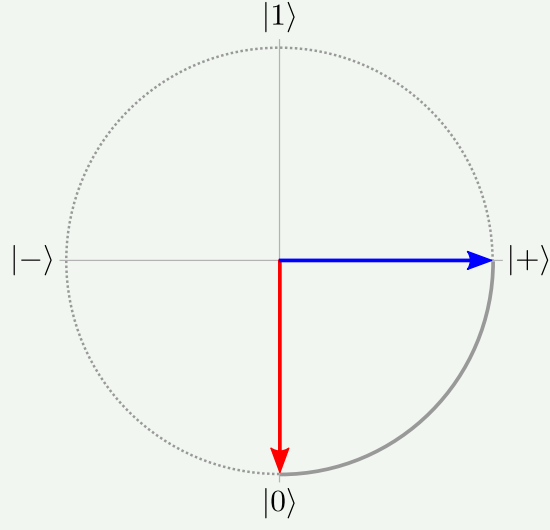
While the optimal unitary operation for maximal ergotropy extraction,

$$U = \sum |\epsilon_j\rangle\langle r_j|, \quad (2.15)$$

always exists, this formal assignment by itself does not prescribe the actual evolution in the spirit of Equations (2.1) and (2.2). There are infinitely many possible evolutions which lead to maximal work extraction. In order to single one of them out as more desirable than others an additional criterion is required. This will be the topic of Chapter 3 where the power of unitary processes is examined as a possible such criterion.

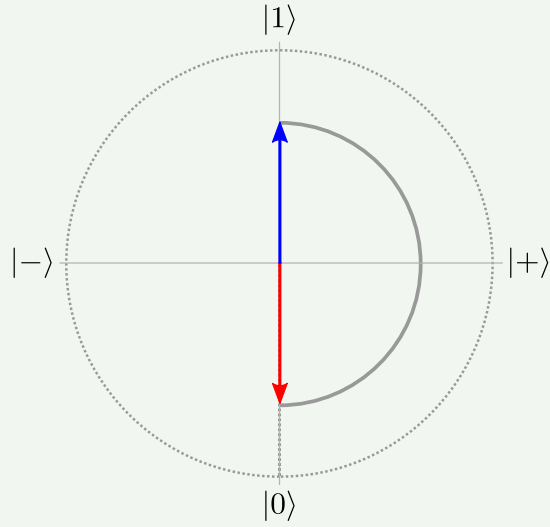
Example 2.2: Ergotropy extraction

Ergotropy encodes extractable work stored in both coherence and excitations (population inversion). We illustrate this for a qubit with the reference Hamiltonian $H = |1\rangle\langle 1|$ on a cut through the x/z -plane of the Bloch sphere. Here, the blue arrows represent the initial active states, the red ones indicate the resulting passive states after ergotropy extraction. The thick grey lines depict the unitary geodesics between the states – that is, the shortest path along which unitary work extraction may occur.



$$\rho = |+\rangle\langle +| \rightarrow \pi = |0\rangle\langle 0|, \\ \mathcal{W} = \frac{1}{2}$$

Figure 2.1: Ergotropy extraction from *coherence* of a pure state ($|+\rangle \equiv \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle)$).



$$\rho = \frac{1}{3}|0\rangle\langle 0| + \frac{2}{3}|1\rangle\langle 1| \rightarrow \pi = \frac{2}{3}|0\rangle\langle 0| + \frac{1}{3}|1\rangle\langle 1|, \\ \mathcal{W} = \frac{1}{3}$$

Figure 2.2: Ergotropy extraction from *excitation* in a mixed state.

In general, ergotropy is not due to either excitations or coherence exclusively but encapsulates a combination of both. In Figure 2.2, for instance, a situation analogous to Figure 2.1 arises half-way through the work extraction process.

2.2.1 Comparison of activities

When considering two different active states, ρ and σ , which share the same internal energy ($\text{tr}[(\rho - \sigma)H] = 0$) it is not generally possible to say which has the higher ergotropy without taking the specific energy eigenvalues of the reference Hamiltonian H into account. It does not generally suffice to know the energy eigenbasis and the order of the energy levels. There are, however, cases where the activities of two different states ρ and σ can be compared without specific consideration of the Hamiltonian's eigenvalues:

- **qubits.** Any passive qubit state is automatically thermal at some inverse temperature β : for two populations $p_0 \geq p_1$ and associated energy levels $\epsilon_0 \leq \epsilon_1$ there always exist β and F such that for $j \in \{0, 1\}$, $p_j = e^{-\beta(\epsilon_j - F)}$ and $\sum p_j = 1$.
- **majorisation** (cf. Box 2.3 and [Marshall et al., 2011]). If the eigenvalues of ρ majorise those of σ – i.e., $\rho \succ \sigma$, and both share the same average energy ($\text{tr}[\rho H] = \text{tr}[\sigma H]$) it must hold that $\mathcal{W}(\rho, H) \leq \mathcal{W}(\sigma, H)$.

Box 2.3: Majorisation

Consider two ordered probability distributions $\mathbf{p} = \{p_j\}$ and $\mathbf{q} = \{q_j\}$ over the same number of events N (i.e., $p_j \geq p_{j+1} \forall j \leq N$ and, equally, $q_j \geq q_{j+1} \forall j \leq N$). The distribution $\mathbf{p}$ majorises $\mathbf{q}$, written as $\mathbf{p} \succ \mathbf{q}$ or $\mathbf{q} \prec \mathbf{p}$, if and only if

$$\sum_j^k p_j \geq \sum_j^k q_j \quad \forall k \leq N. \quad (2.16)$$

This definition is easily extended to quantum states by comparing their spectra (i.e., $\rho = \sum p_j |p_j\rangle\langle p_j|$). Notation is equally extended from probability distributions to states in a straightforward fashion, i.e., $\rho \succ \sigma$.

Example 2.3 illustrates three simple lemmata about majorisation:

1. Pure states majorise all other states.
2. Maximally mixed states are majorised by all other states.
3. For some sets of states no majorisation relations exist: No state majorises any other state in such a set.

Example 2.3: Majorisation

We illustrate majorisation [Marshall et al., 2011] for the case of four normalised probability distributions over three distinct events (i.e., four commuting qutrits).

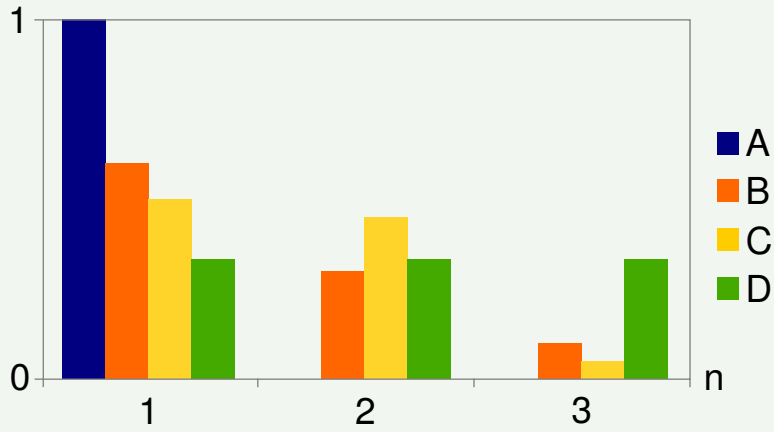
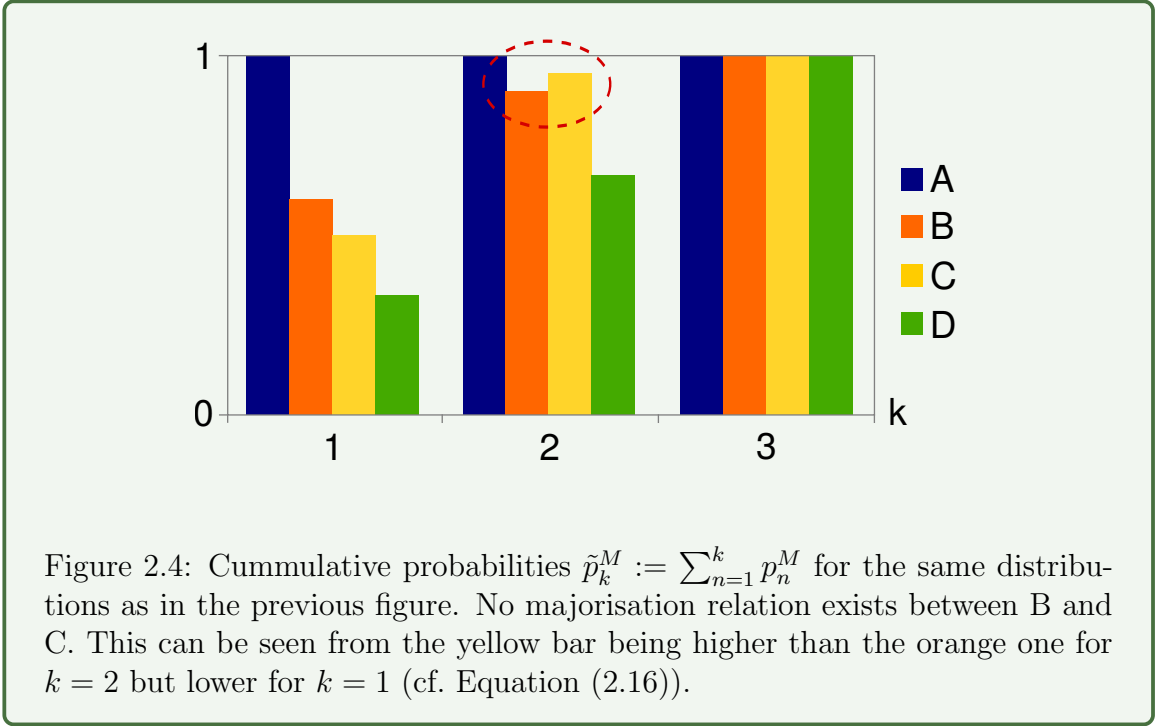


Figure 2.3: Four different, ordered qutrit probability distributions p_n^M (with $M \in \{A, B, C, D\}$). Distribution A corresponds to a pure state and distribution D corresponds to a maximally mixed state.



Majorisation is also useful when comparing passive states: if two states $\pi_1 \succ \pi_2$ are passive with respect to the same Hamiltonian, π_1 is always less energetic than π_2 . This observation is relevant when considering quantum systems as energy storage devices. In that context majorisation relations between two states determine the relationship between the corresponding battery capacities (cf. Equation (3.3)).

As a trivial consequence of the majorisation condition, we point out that the ergotropy never decreases under decoherence in the energy eigenbasis⁶. In this case coherences are destroyed but there may still be excitations present in the state. For a state $\rho' = D(\rho)$ where $D(\cdot)$ is the superoperator which completely decoheres the state in some basis, we note that it always holds that⁷

$$\rho \succ \rho'. \quad (2.17)$$

⁶In this thesis, when we speak of decoherence, we mostly concentrate on a specific type of decoherence: *dephasing*, which is decoherence in some specific basis – i.e., the energy eigenbasis.

⁷A formal proof of this intuitive statement can be found in Watrous' lecture notes on quantum information theory [2011].

While decoherence in a general basis does not conserve the state's energy, i.e., generally $\text{tr}[(\rho' - \rho)H] \neq 0$, in cases where it does it always decreases the ergotropy. This has consequences for the study of battery capacity in the following chapter and for establishing an intuitive thermodynamic meaning of the operational quantities introduced in Chapter 4.

Importantly but perhaps against both physical and mathematical intuition, this statement about the effect of decoherence does not entail a relationship between a state's purity (or entropy) and the ergotropy as is illustrated in Example 2.4.

Example 2.4: Relationship between ergotropy, purity and entropy

We take two passive states

$$\pi = \frac{1}{10} (8 |1\rangle\langle 1| + |2\rangle\langle 2| + |3\rangle\langle 3|), \quad (2.18)$$

$$\pi' = \frac{1}{2} (|1\rangle\langle 1| + |2\rangle\langle 2|). \quad (2.19)$$

Comparing the purities, defined as

$$\mathcal{P}(\rho) := \text{tr}[\rho^2], \quad (2.20)$$

we have

$$\mathcal{P}(\pi) = 0.66 > 0.5 = \mathcal{P}(\pi'). \quad (2.21)$$

Analogously, for the von Neumann entropy (here with $\log_2$):

$$S(\pi) \approx 0.92 < 1 = S(\pi'). \quad (2.22)$$

In order to compare the ergotropies of two active states ρ and ρ' with the same spectra as π and π' , and equal internal energy (i.e., $E = \text{tr}[\rho H] = \text{tr}[\rho' H] > 1$)

we consider the Hamiltonian

$$H = |2\rangle\langle 2| + 9|3\rangle\langle 3|. \quad (2.23)$$

Consequently, $\mathcal{W}(\rho, H) = E - 1 < \mathcal{W}(\rho', H) = E - \frac{1}{2}$ even though $\mathcal{P}(\rho) > \mathcal{P}(\rho')$ and $S(\rho) < S(\rho')$. We conclude:

The ergotropy can increase even under loss of purity or under increase of entropy.

2.2.2 The role of quantum correlations

Consider N copies of a state that is passive but not N -passive: $\pi^{\otimes N}$. Locally, no work can be extracted but the N -fold composition has activated the state and work can be extracted from all N copies collectively in an *entangling operation*. It has been shown [Alicki and Fannes, 2013] that for large N and typical systems the optimal local output states asymptotically approach that thermal state τ_β with the same Shannon entropy as π .

In this N -copy scenario, the optimal global unitary is trivially always an entangling operation: local operations and classical communication (LOCC) operations cannot be used to extract work from a composition of identical passive states. It has been shown, however, [Hovhannisyan et al., 2013] that, given π , it is always possible to obtain optimal work output from the N copies without creating entanglement between the systems at any point during the evolution. This may sound contradictory but is made possible by the fact that an entangling operation need not create entanglement for every possible input state. It was conjectured in the same paper that while evolution through the entangled subspace may not result in an increase of extractable work it will generally permit for a faster process and, accordingly, an increase in power.

The question of increased quantum power due to entangling operations will be the topic of Chapter 3.

Even if the creation of entanglement can be avoided during the evolution, the work advantage from global operations must reflect in the output state as pointed out by Giorgi and Campbell [2015]: the amount of extracted work solely depends on the initial and final state (cf. Equation (2.4)) and does not differ for different evolution paths. Consequently, there is a relation between correlations in the output state and the extractable work. Even for those global work extraction protocols which do not create entanglement during the evolution these correlations appear in the form of quantum discord [Giorgi and Campbell, 2015].

2.3 Context: work extraction in thermodynamics

The question

*How much work can be extracted from a (quantum) thermodynamic system
in a given state?*

has been central to the field of thermodynamics since its early days (as can be seen from Thomson’s formulation of the second law, for instance (cf. Box 1.1 and footnote 6 in Chapter 1)). We have already pointed out that no generic answer exists but will rather depend on what we here refer to as the *rules of the game*. More concretely, one has to specify what mechanisms are permitted for work extraction and, perhaps more crucially, what one considers work in the first place. In this sense, the approach described in this chapter so far is self-contained and complete. We have clearly stated the conditions for the extraction mechanism – unitarity and cyclicity, and Equation (2.14) quantifies the extractable work in an unambiguous way. It is worth noting that the framework employed so far, i.e., Equation (2.4), only considers average quantities. Fluctuations of the work – measured in different experimental runs with

the same ensemble – are not described within this approach. Some of the imposed operational limitations may seem overly restrictive at the present point. Hence, an extension to non-cyclic and non-unitary situations will be presented in Chapter 4.

In spite of the analysis so far being self-contained, we now carefully relate the notion of work extraction presented in the first two sections of the chapter to alternative and complementary scenarios. In particular, we address work extraction in classical, macroscopic thermodynamics in the following section. Subsequently, the consideration of finite-size systems gives rise to study of fluctuations and fluctuation theorems and allows us to introduce the notion of *single shot thermodynamics*. Furthermore, we describe the resource theoretic approach to thermodynamics via the vehicle of *thermal operations*. Finally, we introduce the general, fully quantum approach known as local effective measurement basis (LEMBAS) principle in order to draw a relation to specific results about the role of quantum coherence in work extraction. This canvassing of approaches allows us to return to a more general characterisation of the approach introduced in the first part of this chapter.

Most of these topics are vast and established research fields in their own right. A fully rigorous and general treatment of this extensive wealth of scientific work would go beyond the scope of this thesis and we content ourselves with stating the relevant main results. Further details can be found in the cited publications.

In this section, we express all relationships in quantum language from the beginning even where their thermodynamic meaning is not firmly established in the quantum regime (i.e., if coherences in the energy eigenbasis are present). Furthermore, this section is phrased with a view to work extraction but the majority of concepts apply to a wider range of thermodynamic processes: regardless of specific work extraction protocols, these concepts provide general and complementary frameworks to describe thermodynamic processes from a quantum information theoretic viewpoint.

2.3.1 Macroscopic thermodynamics

In macroscopic thermodynamics, any energy change in a reversible process is generally given by Equation (1.21). Ignoring a potential exchange of particles, the incremental work may be expressed as the sum of infinitesimal displacements against generalised forces [Balian, 1991a]:

$$\delta W = \sum_j \Phi_j dX_j = dU - \beta^{-1} dS. \quad (2.24)$$

It is equal to the incremental change in internal energy minus the heat (which is associated with a change in entropy). In particular, the work of a thermo-adiabatic process ($dS = 0$) is equal to the internal energy change dU . In analogy, the same holds for a unitary quantum process as pointed out above.

In the macroscopic regime, work extraction is often considered for specific reversible scenarios where certain macrovariables (e.g. temperature or pressure) are kept constant by use of corresponding reservoirs. The work that can be extracted in a reversible process is sometimes referred to as *exergy* [Honerkamp, 2012]. For specific choices of reservoirs this leads to the notion of thermodynamic potentials such as the free energy (which corresponds to an isothermal process at inverse temperature β). In fact, the ergotropy introduced above may be understood as a form of exergy or free energy in this sense, albeit in a scenario that acknowledges both the finite size as well as the quantum nature of the system under study.

It has been recognised⁸ that the extractable work can be written in the language of information theory by reference to the relative entropy⁹ introduced in Equation (1.6):

$$R(\rho||\sigma) := \text{tr}[\rho \log \rho] - \text{tr}[\rho \log \sigma]. \quad (1.6)$$

⁸See [Procaccia and Levine, 1976; Donald, 1987] and references therein.

⁹The relative entropy is called Kullback-Leibler divergence in the case of diagonal states (as in the present context) [Kullback and Leibler, 1951]. Here, we represent both quantities as $R(\rho||\sigma)$ and think of classical probability distributions as diagonal density operators.

In the case of a thermostat (a heat bath at temperature β) being the sole reservoir coupled to the system, the difference in Helmholtz free energy $F := E - \beta^{-1}S$ is recovered:

$$\frac{1}{\beta}R(\rho||\tau_\beta) = F(\rho) - F(\tau_\beta) = \text{tr}[\rho H] - \frac{1}{\beta}S(\rho) - \frac{1}{\beta}\log Z \quad (2.25)$$

where $S(\cdot)$ is the von Neumann entropy and Z the partition sum of τ_β . More generally, given multiple reservoirs (including a thermostat) which take the system to a diagonal equilibrium state¹⁰ σ_β the extractable work is given by $\beta^{-1}R(\rho||\sigma_\beta)$ ¹¹.

It is important to recognise that the free energy difference only provides an upper bound on the amount of work which is actually extracted (see Box 2.4). This bound is saturated by reversible processes and it is a manifestation of the second law as pointed out in the previous chapter.

These free energy considerations in macroscopic thermodynamics unfortunately do not directly translate to the finite-size, quantum regime for two reasons:

- I) The role of fluctuations has so far been neglected in this section: if a macroscopic system undergoes a thermodynamic work extraction transformation the measured work in a given experimental run will be only negligibly different from the average value after many runs. This is not the case for finite-size systems where the acknowledgement of fluctuations between the average and a single run gives rise to fluctuation theorems on the one hand¹² and to so-called *single shot* thermodynamics on the other hand. The latter is based on scrutiny of what should

¹⁰We may state the collective effect of a number of reservoirs by specifying the corresponding equilibrium state without reference to the specific equilibration dynamics.

¹¹It was shown by Deffner and Lutz [2010, 2013c] that this quantity, which may be interpreted as *irreversible entropy change* $\Delta S_{ir} := R(\rho||\tau_\beta)$ in the context of fluctuation theorems (Section 2.3.2), possesses a lower bound in terms of the Bures angle (cf. Box 3.2) between the states ρ and τ_β . This relationship in turn allows for the establishment of a lower bound of the irreversible entropy production rate [Deffner and Lutz, 2010].

¹²The most notable ones [Bochkov and Kuzovlev, 1977; Jarzynski, 1997; Crooks, 1999; Kurchan, 2000; Tasaki, 2000] have been reviewed by Esposito et al. [2009] and Campisi et al. [2011].

be considered work in the first place when fluctuations are present [Åberg, 2013]. Complementarity of both of these viewpoints has recently been highlighted and discussed [Yunger Halpern et al., 2015].

- II) The role of coherences requires a more careful treatment. For instance, it is not obvious that the generalisation from the Shannon entropy in the Hamiltonian's eigenbasis to von Neumann entropy and, in the same way, the generalisation from the Kullback-Leibler divergence to the quantum relative entropy are actually thermodynamically meaningful. This fact has been recognised early on [Donald, 1987].

Before we move on to addressing both of these shortcomings inherent to macroscopic considerations of work extraction, we highlight a characterisation of work extraction regimes that was illustrated by Korzekwa et al. [2015]. It helps to categorise the different approaches in four different regimes. The authors classify the different regimes by two characteristics. (A) They differentiate between protocols that are performed in a *single shot* or over many runs. (B) They recognise that approaches to work extraction differ in considering either a single system that is processed at a time or many identical copies of the system which are processed collectively. If according to property (A) one considers processing over many runs this is understood as being equal to considering averages of the relevant quantities, i.e., work, as is the case for the considerations in this thesis. Collective processing (B), on the other hand, assumes many identical copies to be present at the same time. This is not generally assumed here but is crucial to the derivation of thermality, presented the beginning of this chapter (and in Appendix A), where the role of quantum correlations in ergotropy extraction was discussed.

In order to address point (I) from above we now highlight two ways in which the fluctuating nature of finite-size work extraction protocols are commonly taken into

account: fluctuation theorems (Section 2.3.2 and Box 2.4) and single shot thermodynamics (Section 2.3.3). Point (II) is then addressed in Section 2.3.4.

2.3.2 Fluctuation theorems

Fluctuation theorems exist for quantities like work, heat, entropy, and others. With a view to work extraction, the relevant results are summarised in Box 2.4¹³.

Box 2.4: Work fluctuation theorems

Consider a thermal state τ_β that undergoes unitary evolution of duration T caused by a time dependent Hamiltonian $K(t)$. The initial Hamiltonian which determines the spectrum of τ_β is $H \equiv K(0)$ and the output Hamiltonian is $H' \equiv K(T)$. If, in a given experimental run, an energy measurement at the beginning of the protocol determines the system's internal energy to be E and a measurement at the end – with respect to H' – determines the final energy to be E' the work for this run is given by the difference $W = E' - E$. Thus, the forward probability $p_F(W)$ for each value W to occur in a given run can be recorded.

Alternatively, the work may be measured with respect to the same Hamiltonian at the beginning and at the end of the protocol. This view is outlined at the end of this box.

Now consider the reverse (unitary) protocol where the system starts in a thermal state τ'_β of the final Hamiltonian H' but at the same temperature β as before. In analogy to the forward case the reverse probabilities $p_R(-W)$ can thus be recorded, allowing for a derivation of *Crooks' theorem* [Crooks, 1999; Tasaki, 2000]:

$$\frac{p_F(W)}{p_R(-W)} = e^{\beta(W - \Delta F)}. \quad (2.26)$$

¹³This section adopts the sign convention of considering work *done* rather than *extracted*.

Here, ΔF is the free energy difference between τ'_β and τ_β . The difference in the exponent on the right-hand side is called *dissipated work* [Jarzynski, 2011]

$$W_{diss} := W - \Delta F. \quad (2.27)$$

It is also often referred to as heat because it is associated with irreversibility of the process [Gomez-Marin et al., 2008]: the dissipated work is the amount of energy that would get transferred to a heat bath in a subsequent thermalisation stage. The implicit assumptions that have gone into stating Crooks' equality are Markovianity (no correlations with the implicitly involved reservoirs), on the one hand, and microreversibility – a mathematical condition on time-reversibility of the unitary evolution operator – on the other [Campisi et al., 2011].

Re-arrangement and integration over W yields *Jarzynski's equality* [Jarzynski, 1997; Kurchan, 2000]

$$\langle e^{-\beta W_{diss}} \rangle = 1 \quad (2.28)$$

for the forward process.

The power of these fluctuation theorems lies in them establishing an exact relationship between the equilibrium quantity ΔF and the statistics of the fluctuating, single-run quantity W . Hence, a suitably designed experiment may be used to infer the equilibrium properties of a quantum system by studying its out-of-equilibrium behaviour [Mazzola et al., 2013; Dorner et al., 2013; Batalhão et al., 2014; Roncaglia et al., 2014; De Chiara et al., 2015].

As a further lemma from Jarzynski's equality, the free energy difference is established as upper bound to the average work by applying Jensen's inequality

to the exponential^a:

$$\langle W_{diss} \rangle \geq 0 \Rightarrow \langle W \rangle \geq \Delta F. \quad (2.29)$$

Thus, a statement of the second law is obtained as a consequence of the analytically exact equalities due to Crooks and Jarzynski when considering work fluctuations. Here, statistical irreversibility is a consequence of the asymmetry inherent to the consideration of an initial equilibrium state at the beginning of the protocol^b.

Inclusive vs. exclusive work

A further classical work fluctuation theorem by Bochkov and Kuzovlev [1977] relies on a different definition of work^c which corresponds to making the second energy measurement at the end of the process with respect to the initial Hamiltonian H . Calling this single-run work *exclusive work* W_0 (and, conversely, W in the above definition *inclusive work*) [Jarzynski, 2007; Campisi et al., 2011] the *Bochkov-Kuzovlev fluctuation theorem* can be derived [Bochkov and Kuzovlev, 1977; Campisi et al., 2011]:

$$\langle e^{-\beta W_0} \rangle = 1. \quad (2.30)$$

In the case of a cyclic process (i.e., $H' = H$) this equation is identical to the Jarzynski equality (Equation (2.28)).

^aCf. footnote 13 for sign convention: with negative signs for W and ΔF the inequality sign in Equation (2.29) also flips around.

More generally, the dissipated work can be expressed in terms of the Kullback-Leibler divergence between probability distributions of forward and reverse trajectories [Gomez-Marin et al., 2008; Jarzynski, 2011].

^bThis irreversibility, which manifests as entropy production (cf. footnote 11), has recently been demonstrated experimentally [Batalhão et al., 2015].

‘It should be noted that Bochkov and Kuzovlev [1977] only speak of ‘change in internal energy’ in their original paper. The identification of this energy change with work was only made in later works.

It is important to note the assumptions that are made when deriving the fluctuation theorems. They are: (1) initial (thermal) equilibrium, and (2) microreversibility. It is in particular the first one of these assumptions that has been challenged [Allahverdyan and Nieuwenhuizen, 2005; Allahverdyan, 2014] owing to the desire to be able to describe work for non-diagonal initial states. The viewpoint of ascribing work to two energy measurements, and hence disregarding any initial coherence in the energy eigenbasis, arguably prohibits a full extension of classical fluctuation theorems from fully capturing quantum thermodynamic processes [Kammerlander and Anders, 2015].

2.3.3 Single shot thermodynamics

Single shot work extraction stems from the notion that ‘work-like’ energy should not be defined as an average over many experimental runs but rather in a single experiment. We may classify the corresponding literature in two main categories: work extraction ‘games’ and a resource theoretic approach, giving rise to the concept of so-called *thermal operations*.

Work extraction from information

Single shot work extraction processes are often phrased as games and inspired by the thought experiments of *Maxwell’s demon* [Maxwell, 1902; Brillouin, 1962; Leff and Rex, 2003; Maruyama et al., 2009], *Szilard’s engine* [Szilard, 1929; Brillouin, 1962; Leff and Rex, 2003], and *Landauer’s erasure* [Landauer, 1961]. In these approaches [Dahlsten et al., 2011; Åberg, 2013], work extraction from a state which commutes with the Hamiltonian is done by an agent who can exploit information about the system

in order to achieve a certain outcome. Systems are often, but not always, allowed to be processed collectively in order to achieve a certain work output. These treatments give rise to expressions for the amount of work that can be extracted deterministically or with a small probability of failure ϵ and highlight the importance of single-shot entropies such as the so-called min- and max-entropies [Renner, 2005; Datta, 2009] and smooth entropies [Renner and Wolf, 2004; Renner, 2005; Datta, 2009] respectively.

The resource theoretic framework: thermal operations

Another single-shot framework which tends to be phrased rather differently from those scenarios discussed in the previous paragraph are thermal operations. They arise in the context of resource theoretic approaches to quantum thermodynamics [Janzing et al., 2000; Horodecki and Oppenheim, 2013; Brandão et al., 2013; Gour et al., 2015] and represent those operations that are understood as being freely available. A precise definition of thermal operations is given in Box 2.5.

Box 2.5: Thermal operations

Given an input state ρ and a corresponding reference Hamiltonian H , thermal operations $\mathcal{O}_\beta$ allow for:

1. Free access to a thermal ancilla in state τ_β (with corresponding reference Hamiltonian G at some fixed inverse temperature β):

$$\rho \otimes \tau_\beta. \tag{2.31}$$

2. Joint, energy-conserving, unitary evolution of system and ancilla:

$$U\rho \otimes \tau_\beta U^\dagger; \tag{2.32}$$

Here, U is an evolution operator on the composite system and energy conservation is ensured by requiring

$$[U, H \otimes \mathbf{I} + \mathbf{I} \otimes G] = 0; \quad (2.33)$$

3. Discarding of the post-evolution ancilla state:

$$\rho' = \text{tr}_A[U\rho \otimes \tau_\beta U^\dagger], \quad (2.34)$$

where tr_A indicates a partial trace over the Hilbert space associated with the ancilla.

This framework naturally incorporates the possibility of including further external systems (in addition to the thermal ancilla). In particular, a clock system and a work reservoir may equally be included in the description [Horodecki and Oppenheim, 2013; Skrzypczyk et al., 2014; Frenzel et al., 2014; Malabarba et al., 2015]. Global energy conservation is then imposed in the same fashion as above by taking all systems into account when requiring the commutator in Equation (2.33) to vanish.

Thermal operations have a couple of interesting properties which merit a separate mention:

- The temperature β is assumed to be fixed and defines a set of thermal operations specific to that temperature. Physically, this corresponds to a scenario where one single, infinite, thermal heat bath is available. In physical settings where more than one thermal heat bath is available one can describe serial interaction with those heat baths with thermal operations corresponding to different temperatures β_1, β_2 , etc. The description of parallel interaction with two or more

heat baths at different temperatures, say in a continuous or two-stroke engine, is not possible within this paradigm¹⁴.

- Thermal operations preserve the thermal state at inverse temperature β (but generally not at $\tilde{\beta} \neq \beta$):

$$\rho = \tau_\beta \rightarrow \rho' := \text{tr}_A[U\rho \otimes \tau_\beta U^\dagger] = \tau_\beta. \quad (2.35)$$

This property makes them a subset of so-called *thermal maps*¹⁵ (also referred to as *Gibbs-preserving maps*) which are defined as those maps M_β which have the thermal state τ_β as fixed point:

$$M_\beta(\tau_\beta) = \tau_\beta. \quad (2.36)$$

It has been demonstrated by Faist et al. [2015] that thermal operations are in fact a strict subset of thermal maps: there exist thermal maps which cannot be implemented by thermal operations.

¹⁴A resource theorist might argue that even in conventional engines, which operate between two heat baths at different temperatures, at most one of these heat baths is a free resource: the other one needs to be heated by expending energy (e.g. by burning some fuel such as petrol or coal). This argument, however, would not satisfy an engineer who might point out that it does not in fact apply generally. Examples of conventional, ‘real world’ engines where two heat baths at different temperatures may be considered ‘free’ include geothermal power stations (which harness hotter temperatures a few kilometers below the Earth’s surface) and engines which harness solar radiation as heat bath. In the strict sense, both of these energy sources are of course finite and due to underlying nuclear mechanisms but they certainly seem unlimited in practical terms (i.e., on time spans comparable to the existence of the human species).

¹⁵We point out that there is a subtle but crucial difference between *thermal maps* and their strict subset called *thermalising maps*. The former have the property that they preserve at least one thermal state τ_β at a given temperature β for a given reference Hamiltonian H . By virtue of the *data processing inequality*

$$R(\rho||\sigma) \geq R(M(\rho)||M(\sigma)),$$

which holds for all CPTP maps M , the relative entropy between the system state and a fixed point of the map never increases [Lindblad, 1975]. The cases where equality holds, however, are crucial here: not all *thermal maps* will actually thermalise all states (A given thermal map could, for instance, have further fixed points. Even more trivially, the identity operation will preserve a thermal state but not take other states towards it). In contrast, *thermalising maps* are those which strictly take any input state to a thermal state.

2.3.4 The role of coherence

In quantum thermodynamics, the Hamiltonian H singles out a natural basis of Hilbert space. Consequently, quantum coherence (which is always contingent on the choice of basis) plays an important role when considering thermodynamics of finite-size quantum systems. Any phenomena related to coherence between energy eigenstates will have no counterpart in classical physics and it is arguably state properties like coherence which render studies in quantum thermodynamics truly quantum. However, explicit studies of the influence of coherence in work extraction scenarios has only recently been addressed in more depth. Up until now, no complete picture has emerged as to the thermodynamic role of coherence. Despite using the language and notation of quantum physics in this section, so far, we have not explicitly taken coherence into account and diagonal states have been considered for the most part¹⁶. In the quantum thermodynamics literature coherence has been addressed in two ways: explicitly within the resource theory framework and implicitly by adopting a fully quantum view of thermodynamic processes. We first address the first approach before describing the second in Box 2.6.

Consider the example of Figure 2.1: if no driving $V(t)$ occurs, the initial state will rotate around the z -axis under the action of the reference Hamiltonian $H = |1\rangle\langle 1|$. If the interaction $V(t)$ is then turned on at some time $t_0 > 0$, the work extraction process will be affected by the delay t_0 and it will generally not be optimal any more. In other words, unitary work extraction as described in this chapter is not invariant under time-translation with $U_t = \exp[-iHt_0]$. This is not the case for thermal operations which in fact ‘commute’¹⁷ with such time-translation unitaries [Lostaglio

¹⁶The resource theoretic approach in the previous section specifically allows for general quantum states. However, the understanding of energy conservation inherent to Equation (2.33) effectively prohibits any operational significance of quantum coherence: the corresponding work is ‘locked’ as a consequence of time-translation invariance. The following paragraph clarifies this point.

¹⁷‘Commutation’ is here understood in the sense that the same output state results regardless of when the time-translation is applied – before or after the thermal operation. It is in this sense that thermal operations are invariant under time-translation.

et al., 2015a] as a consequence of the strict energy conservation requirement imposed by Equation (2.33). This correspondence between time-translation invariance and energy conservation may in fact be understood as a consequence of Noether’s famous theorem [1918] [Marvian and Spekkens, 2014]. Under strict energy conservation, the same amount of work can be extracted from a single copy of a state ρ as from $D(\rho)$ – the same state fully dephased in the energy eigenbasis [Skrzypczyk et al., 2014], in effect rendering coherences operationally meaningless in this scenario. However, following the realisation that a coherence reference can provide a useful catalyst for work extraction [Åberg, 2014], Lostaglio et al. [2015a,b] have suggested that coherence should be considered a resource in addition to generalised notions of free energy [Brandão et al., 2015] which apply to thermal operations.

In an alternative approach to thermal operations the full dynamics of a larger system may be considered in order to derive an effective local dynamics. This approach equally captures the effect of coherence, albeit implicitly. It is outlined in Box 2.6.

Box 2.6: The local effective measurement basis (LEMBAS) principle

The acronym *LEMBAS* is short for *Local Effective Measurement Basis* [Weimer et al., 2008; Gemmer et al., 2009; Mahler, 2014]. In this approach, two interacting systems, A and B , are considered. Both systems – in particular B in the present context – may in turn be composed of a set of subsystems (i.e., with different associated thermodynamic roles). The energy exchange between A and B is to be split up into work and heat. In order to achieve this, the local effective measurement basis (LEMBAS) approach proceeds in two main steps:

- 1) A local dynamics is derived for the system of interest (here: system A).
- 2) An effective, local basis is chosen. Energy changes of the system are measured with respect to this basis.

In order to derive the local dynamics on A , without loss of generality, the total Hamiltonian is first decomposed as

$$H_{AB} = H_A \otimes \mathbf{I}_B + \mathbf{I}_A \otimes H_B + V_{AB}. \quad (2.37)$$

That is, $H_{A/B}$ are local to each subsystem and V_{AB} acts on both. Importantly, no a priori restrictions are made – neither on V_{AB} nor on the systems themselves (e.g. by requiring a large size or similar). Without loss of generality, the global state at any given time can formally be written as

$$\rho_{AB} = \rho_A \otimes \rho_B + \gamma_{AB}. \quad (2.38)$$

Here, $\rho_{A/B} = \text{tr}_{B/A}[\rho_{AB}]$ are the local, reduced states of the system while γ_{AB} are the correlations that would get ‘lost’ in the partial traces. Note that in this approach all original contributions to the Hamiltonian (i.e., H_A , H_B , and V_{AB}) may be taken to be time-independent. Time-dependence enters into the local states $\rho_{A/B}$, the correlations γ_{AB} , and consequently the effective local Hamiltonians. We only explicitly indicate time-dependence in the Hamiltonians but not in the states which are in principle all time-dependent.

Designating subsystem A the system of interest, one may derive an effective equation of motion for the local state ρ_A . This assignment is reminiscent of the standard, microscopic derivation of master equations [Breuer and Petruccione, 2002] but, importantly, does not make the *Born-Markov* approximation.

$$\begin{aligned} \dot{\rho}_A &= \text{tr}_B[\dot{\rho}_{AB}] \\ &= -i \text{tr}_B [[H_{AB}, \rho_{AB}]] \\ &= -i ([H_A, \rho_A] + [\text{tr}_B[(\mathbf{I}_A \otimes \rho_B)V_{AB}], \rho_A] + \text{tr}_B[[V_{AB}, \gamma_{AB}]]) . \end{aligned} \quad (2.39)$$

Here, a dot indicates a derivative with respect to time. The step from the first to the second line makes use of the von Neumann equality of the total system; the step from the second to the third line is slightly cumbersome but straightforward: it employs no approximations. This motivates the following definition:

$$\Delta H_A(t) := \text{tr}_B[(\mathbf{I}_A \otimes \rho_B)V_{AB}]. \quad (2.40)$$

In order to determine the energy change that comes with the effective local evolution a local effective measurement basis (LEMBAS) has to be chosen. This choice is not further elaborated upon by its proponents who choose H_A as LEMBAS [Weimer et al., 2008; Gemmer et al., 2009; Mahler, 2014; Hosseini-Nejad et al., 2015]. Subsequently, the chosen basis is taken into account by further dividing $\Delta H_A(t)$ into a part $\Delta H_A^{\parallel}(t)$, which commutes with H_A , and another part, $\Delta H_A^{\perp}(t)$, which does not. The energy eigenbasis at a given time is then understood to be determined by the effective Hamiltonian

$$H_A^{eff}(t) := H_A + \Delta H_A^{\parallel}(t) \quad (2.41)$$

(or, simply, by H_A , which commutes with $H_A^{eff}(t)$ by definition). More generally, one may also choose an alternative basis and $H_A^{eff}(t)$ would be determined accordingly. At any rate, it is the recognition of this effective local Hamiltonian that introduces effective time-dependence into the problem (in addition to any time-dependence that may have originally been present in H_A , H_B , V_{AB} which are here, as in other treatments of the LEMBAS principle, considered time-independent).

Calculating the infinitesimal change of the internal energy in this basis we obtain

$$\begin{aligned}\dot{E} &= \frac{d}{dt} \text{tr}[H_A^{eff}(t)\rho_A] \\ &= \underbrace{\text{tr}[(\Delta \dot{H}_A^\parallel(t) - i[H_A^{eff}(t), \Delta H_A^\perp(t)])\rho_A]}_{=:\dot{W}} - \underbrace{i \text{tr}[H_A^{eff}(t) \text{tr}_B[[V_{AB}, \gamma_{AB}]]]}_{=:\dot{Q}}\end{aligned}\quad (2.42)$$

The splitting of the total energy change into work and heat contributions is here motivated by the realisation that it is the state change corresponding to the second term which contributes to the change in (von Neumann) entropy while that associated with the first term does not:

$$\begin{aligned}\dot{S}_A &= -\text{tr}[\dot{\rho}_A \log \rho_A] - \text{tr}[\rho_A \frac{d}{dt} \log \rho_A] \\ &= i \text{tr}[\text{tr}_B[[V_{AB}, \gamma_{AB}]] \log \rho_A].\end{aligned}\quad (2.43)$$

In the following section, we use the view inherent to the derivation of the LEMBAS principle in order to point out the assumptions which allow for an effective embedding of unitary work extraction in a larger, time-independent ‘universe’.

2.3.5 Relation to unitary work extraction

The preceding introduction and discussion of various work extraction frameworks in (quantum) thermodynamics is not motivated by encyclopedic ambitions but much rather provides some contextual ground on which we now proceed to discuss the approximations, assumptions, and interpretations which are inherent to the understanding of thermodynamic work extraction in this thesis: work due to external driving with a time-dependent Hamiltonian $K(t)$.

With the definitions of both thermal operations and the LEMBAS framework in mind, we now relate these concepts back to the approach applied here which

considers the thermodynamic control of the system as being due to a time-dependent Hamiltonian $K(t)$. The marked difference is that both the LEMBAS approach and thermal operations explicitly model the system itself as well as external reservoirs (i.e., heat bath, work reservoir, etc.) while the time-dependent Hamiltonian approach makes an effectively semi-classical approximation by considering all external effects to be captured in the Hamiltonian dynamics. This differentiation applies in the same sense to the extension of the Hamiltonian dynamics to more general processes in Chapter 4. We are now guided by the following two questions:

- *How can system dynamics described by $K(t)$ be derived from the LEMBAS approach or from thermal operations?*
- *How does the energy accounting according to a reference Hamiltonian H compare to the LEMBAS principle where an effective Hamiltonian $H_A^{eff}(t)$ provides the energy reference?*

We stress again that the approach outlined in the first two main sections of this chapter – and extended in Chapter 4 – is in itself self-contained but we find it important to clearly explain the relationship to other frameworks in order to provide an appropriate context for this work.

Expression as subsystem of an isolated ‘universe’

For comparison we express again the infinitesimal work due to a time-dependent Hamiltonian $K(t) = H + V(t)$ (cf. Equations (1.13) and (1.14)):

$$\dot{W} = \frac{d}{dt} \text{tr}[\rho K(t)] = \text{tr}[\dot{\rho} K(t)] + \text{tr}[\dot{V}(t) \rho] = \text{tr}[\dot{V}(t) \rho], \quad (2.44)$$

where, as before, the last equality follows from the von Neumann equality. This assignment of what should be considered work differs from the one derived with the choice of LEMBAS in Box 2.6. It may, however, be reconciled with the LEMBAS

principle by identifying $V(t) := \Delta H_A(t)$ and choosing the eigenfunctions of $K(t) = H + V(t) = H_A + \Delta H_A(t)$ as LEMBAS (rather than those of H_A). In this case the definitions of work coincide and we may re-express Equation (2.42) accordingly¹⁸:

$$\dot{E} = \frac{d}{dt} \text{tr}[K(t)\rho_A] = \underbrace{\text{tr}[\dot{V}(t)\rho_A]}_{=:\dot{W}} \underbrace{-i\text{tr}[K(t)\text{tr}_B[[V_{AB}, \gamma_{AB}]]]}_{=:\dot{Q}} \quad (2.45)$$

Now the work equals the total energy change if no correlations γ_{AB} develop between systems A and B – or, more generally, if the correlations remain diagonal in the eigenbasis of V_{AB} .

Cyclicity may additionally be imposed and corresponds to demanding that energies be measured with respect to the same reference Hamiltonian at the beginning and at the end of the protocol¹⁹. Formally, any evolution can be made cyclic by adding a *sudden quench* – an abrupt change of Hamiltonian parameter(s) – at the end of the protocol, such that the driving Hamiltonian is returned back to the original reference Hamiltonian, leaving the system state unaffected in the process. In Equation (2.1), which expressed the driving Hamiltonian of a cyclic process as $K(t) = H + V(t)$, one would in this spirit formally allow for $V(T) \neq 0$ and then add a quench $V(T) \rightarrow 0$ at the end of the protocol. In this case, the analogues of inclusive and exclusive work coincide.

We may now characterise the approach of describing a thermodynamic process in terms of a local time-dependent Hamiltonian $K(t)$ as a semi-classical approximation in

¹⁸Coming from the ambition to derive an effective local description from a larger time-independent Hamiltonian picture the operational meaning of this LEMBAS may seem debatable since it differs from the original basis given by H_A . From the inverse viewpoint, however, i.e., describing the embedding of an operational local control in a larger Hamiltonian dynamics, $K(t)$ actually appears as the natural choice of basis.

¹⁹This is analogous to the difference between *inclusive* and *exclusive* work encountered in the study of work fluctuation theorems [Jarzynski, 2007; Campisi et al., 2011]. Importantly, the notions are only an analogy, however, and do not coincide with the present case if the initial states are allowed to possess coherence in the energy eigenbasis: work extraction scenarios studied in the context of fluctuation theorems such as the ones introduced in Box 2.4 are phrased in terms of two energy measurements, the first of which destroys any coherence in the initial state.

the sense that it can be derived under assumption of vanishing or diagonal correlations between system and control mechanism. For this reason the implicit work source which absorbs the energy change due to $K(t)$ is often referred to as being macroscopic or classical.

Energy conservation

Turning the attention to thermal operations, it has been pointed out in a very similar fashion (equally presuming no correlations) that a time-dependent picture can effectively be derived by looking at the composition of a larger system, in particular by taking a ‘clock’ system into account [Brandão et al., 2013]. In this context, the additional requirement of strict energy conservation (Equation (2.33)) has to be observed. This strict formulation stems from the more general requirement that energy be conserved globally. That is, following the description in Box 2.5 (in particular Equation (2.34)),

$$\Delta E = \text{tr}[(\text{tr}_A[U\rho \otimes \tau_B U^\dagger] - \rho)(H \otimes \mathbf{I} + \mathbf{I} \otimes G)] = 0. \quad (2.46)$$

If this requirement is to be fulfilled for all possible input states ρ , the evolution operator U has to commute with the sum of the local Hamiltonians, yielding Equation (2.33). In the present context, the equation is fulfilled if the interaction V_{AB} commutes with the local Hamiltonians. Generally, this strict energy conservation will significantly restrict the possible operations (as is generally the case for thermal operations).

It is worth pointing out that global energy conservation may still be upheld in a less strict sense. Since Equation (2.45) does not depend on H_B it is entirely possible, for any given local operation on system A , to conceive of a corresponding operation on B that cancels the energy change (i.e., Equation (2.45) for B would be the same

but negative). Energy conservation in this sense applies to the average but equally fulfils Equation (2.46). It is crucially not a property of the interaction term alone but is additionally contingent on the input state ρ .

Summary

We are now in a position to summarise the assumptions that underlie the association of work with the energy change due to time-dependent Hamiltonian driving:

- 1) In unitary work extraction we consider average work. The work in individual runs may significantly fluctuate in the finite-size regime but will converge on the average over many runs. Nonetheless, the approach is not asymptotic: each system may be processed individually.
- 2) We do not explicitly model the work reservoir. Rather, it implicitly absorbs the energy change as work. In particular:
 - a) Correlations between system A and work reservoir B commute with some implicitly assumed interaction V_{AB} between the two at all times²⁰ (or even vanish):

$$[V_{AB}, \gamma_{AB}] = 0 \ \forall \ t. \quad (2.47)$$

- b) We do not assume strict energy conservation in the sense of Equation (2.33). However, any given work extraction process can always be implemented such that the energy change of the system is cancelled by that of a ancillary system.
- 3) Implicitly, we assume the availability of a clock system in order to make coherences available for work extraction.

²⁰We may relax this restriction further by allowing for a finite heat flux during the evolution (according to Equation (2.45)) but requiring the net heat to vanish over the whole process.

2.3.6 Conclusion

We state again that it may indeed be futile to insist on a single all-encompassing definition of ‘work’ which is not contingent on certain operational constraints (*rules of the game*). The range of applicability of results from macroscopic thermodynamics is well defined but its notions of work and heat do not directly apply outside of the confines built into the framework. It should be no surprise that differing expressions emerge for what is considered work in less constrained scenarios. Nonetheless, we may stress that within each framework one should expect to recover some notion of a ‘second law’ linked to an irreversible increase of entropy, and, in consequence, an appearance of the so-called *arrow of time*. If the dynamics are fully reversible (as for unitary processes) no arrow of time emerges but even in this limit the entropy will not decrease.

Equilibrium thermodynamics derives its relevance not least from its operational usefulness in designing thermal engines and the like²¹. In a similar vein, differing frameworks of work extraction will have to answer to expectations of operational meaning in much the same way. It is not clear that not more than one of them would prove to be meaningful under different, but practically important, *rules of the game*.

In the current context we focus on work extraction associated with external time-dependent driving due to a Hamiltonian $K(t)$. In the following chapter this will allow us to introduce the concept of quantum batteries and to derive results about optimal charging power. In Chapter 4 the notions of work and heat will be generalised to CPTP processes in an operational fashion.

²¹This operational perspective is apparent from the outset in the treatise which started the formal study of thermodynamics: Carnot’s *Réflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance* [1824].

Quantum batteries and powerful unitary processes

“With great power comes great entanglement.”

Quantum-man

Building on the notion of unitary work extraction – introduced in the previous chapter – this chapter addresses the following question:

How much power can be generated in a cyclic, unitary process?

Here, we phrase the problem from the opposite viewpoint as before: starting from a passive state, deposition of work is considered rather than its extraction. The difference between extraction and deposition is only semantic, however, and a question of language. Physically, there is a symmetry between a work extraction process and one that deposits work as long as unitary operations are considered. This will be the case here: the study of non-unitary operations is left to Chapter 4.

In this chapter we first introduce quantum batteries and the notion of power in unitary processes, in a general fashion. In the context of quantum power, we briefly review some results about quantum speed limits. This is followed by an analytical optimisation of single qubit protocols for power. In Section 3.5, we turn the attention towards a multi-partite setting and show by example that entangling operations can yield a significant increase in the power of unitary dynamics. A geometric interpretation of this speedup is explained in the penultimate section, followed by a consideration of the implementability of our results.

This chapter is based on the article [Binder et al., 2015b] and extends the results presented therein. It also highlights some of their implications as well as potential avenues for further research.

The results presented here contribute two original aspects to the research field. The first contribution is a complete protocol for powerful driving of a single qubit, valid for any initial state. The second contribution is a demonstration of power enhancement due to entangling operations (when arrays of quantum batteries are considered). An intuitive explanation which illustrates the origin of this enhancement completes the latter result.

3.1 Quantum batteries

A battery is a physical system that stores energy. In the quantum case, energy can be stored in the energy levels and coherences of a state as illustrated in Example 2.2. Such energy storage is always contingent on some time-independent reference Hamiltonian H . Any quantum system with distinct, and, for practical purposes,

stable¹, energy eigenstates can hence be viewed as a quantum battery. Given the reference Hamiltonian H , the energy stored in a quantum battery in state ρ is then equal to the difference between the system's internal energy $E_\rho = \text{tr}[H\rho]$ and the energy $E_\pi = \text{tr}[H\pi]$ of the energetically lowest, accessible state π , which is passive by definition. In other words: the stored energy equals the ergotropy introduced in Equation (2.14):

$$\mathcal{W} = \text{tr}[H\rho] - \text{tr}[H\pi] \quad (3.1)$$

In order for the battery to be useful, the availability of some level of unitary control over the system is additionally required. This is quite analogous to a conventional battery: it does not fulfil its intended purpose if the only way to extract energy from it is by ‘shortcircuiting’² it so it may emanate heat.

Charging a quantum battery is to change its state from an initial state ρ to a more energetic state ρ' such that $\text{tr}[(\rho' - \rho)H] > 0$. Conversely, using the battery will take it to a lower energy state ρ'' such that $\text{tr}[(\rho'' - \rho)H] < 0$. Here, both charging and discharging processes are restricted to be cyclic and unitary (cf. Box 2.1). Remembering that the energy change in a unitary process must always be considered work, the expressions *work deposition* and *battery charging*, and, equally, *work extraction* and *using the battery* or *discharging* it are used synonymously here.

In summary, a quantum battery is a quantum system with a reference Hamiltonian H . Its total charge is given by Equation (3.1). What differentiates it from other energy storage systems is the possibility of unitary control.

In what follows, the battery's Hilbert space is presumed to be of a finite dimension d . The corresponding Hamiltonian H is consequently always bounded³. This allows for the definition of battery capacity.

¹From an experimental perspective, stability is certainly not a trivial requirement as decay processes such as spontaneous emission affect the quantum battery.

²When the two terminals of a conventional electric battery are directly connected, no effect is produced apart from a heating of the (conductive) connector due to its Ohmic resistance.

³In other words: all Schatten p -norms $\|H\|_p$, defined below in Box 3.3, are finite.

Battery capacity

As a consequence of unitarity, the (normalised) spectrum $\mathbf{p} := \{p_i\}$ of any accessible battery state is fixed. Given $\mathbf{p}$ and a Hamiltonian H , we may hence define a *maximally active* state ω : amongst all diagonal states with spectrum $\mathbf{p}$, ω is the one⁴ with the largest energy $E_\omega = \text{tr}[H\omega]$.

Expressing the Hamiltonian $H = \sum_j \epsilon_j |\epsilon_j\rangle\langle\epsilon_j|$ in its increasing spectral decomposition as before ($\epsilon_j \leq \epsilon_{j+1} \forall j: 1 \leq j \leq d$), and given an ordered spectrum $\mathbf{p}$ (with $p_j \geq p_{j+1} \forall j: 1 \leq j \leq d$), the capacity $\mathcal{C}$ of the corresponding battery with respect to cyclic unitary operations is given by the energy difference between the maximally active state

$$\omega = \sum_{j=1}^d p_{d-j+1} |\epsilon_j\rangle\langle\epsilon_j| \quad (3.2)$$

and the passive state $\pi = \sum_j p_j |\epsilon_j\rangle\langle\epsilon_j|$:

$$\mathcal{C} := \text{tr}[H(\omega - \pi)] = \sum_{j=1}^d \epsilon_j (p_{d-j+1} - p_j). \quad (3.3)$$

The capacity depends on the spectrum and the reference Hamiltonian but not on the state of the battery at any given time.

When comparing two different, normalised spectra $\mathbf{p}$ and $\mathbf{q}$ with the property⁵ $\mathbf{p} \succ \mathbf{q}$, we note that $\mathbf{p}$ allows for both a lower minimum-energy state (the passive state π) as well as a higher maximum-energy state (the maximally active state ω) than $\mathbf{q}$. Its corresponding capacity hence exceeds that of a battery with the same reference Hamiltonian but different spectrum $\mathbf{q}$: $\mathcal{C}_{\mathbf{p}} \geq \mathcal{C}_{\mathbf{q}}$.

⁴As before, in the case of passive states, ω is not unique if there are degeneracies in the spectrum of H . However, the results presented here are not changed by such potential degeneracies (as long as H is not fully degenerate, which would render the discussion of quantum batteries pointless) and we consequently allow ourselves to speak of ω as if it were unique.

⁵The concept of majorisation, symbolised as ' $\succ$ ', was introduced in Box 2.3.

For a fixed reference Hamiltonian H , a battery in a pure state consequently always has a higher capacity than one in a non-pure state. A battery in a maximally mixed state trivially has no capacity at all – and hence less than a battery in any other state, since $\mathcal{C}$ is always non-negative by definition.

With the preceding definition of quantum batteries in mind we now consider the power of unitary processes in a general fashion before turning the attention back to quantum batteries and the investigation of how to charge them powerfully.

3.2 Quantum power

The work performed during a general (i.e., non-cyclic), unitary process $(\rho, H) \xrightarrow{U} (\rho', H')$ is given by Equation (2.4):

$$W := \text{tr}[H'\rho' - H\rho]. \quad (3.4)$$

Power, on the other hand, is the work done per time

$$P_{inst}(t) := \frac{d}{dt}W(t) = \frac{d}{dt}\text{tr}[\rho(t)H(t)], \quad (3.5)$$

where time dependence of both state and reference Hamiltonian has been made explicit in the notation. Equation (3.5) expresses what is called *instantaneous power*. Its statement relies on the process being unitary. Considering a process of duration T , the instantaneous power averaged over the whole process duration is the quantity of interest for the current purpose:

$$P := \frac{1}{T} \int_0^T \left(\frac{d}{dt}\text{tr}[\rho(t)H(t)] \right) dt = \frac{W(T)}{T}. \quad (3.6)$$

We will refer to Equation (3.6) as *power* in this chapter. Note that it contains two averages: (1) over time as just pointed out, (2) over energy measurements at the beginning and the end. This second average in turn contains a classical and a quantum part: there is an uncertainty related to the classical ignorance of which energy levels are populated at the beginning and the end of the process and a quantum uncertainty due to coherences in the respective energy eigenbases at the beginning and the end.

Having introduced power for the case of general unitary processes, we return to the previously considered paradigm (Box 2.1) of cyclic, unitary processes in the following. The additional requirement of cyclicity is here rather natural as can be illustrated with a simple example: consider a non-cyclic process such as a sudden quench, $H \rightarrow H'$, which does a finite amount of work on the system in an instant ($T \rightarrow 0$) and therefore produces infinite power (in the limit of the quench being perfectly sudden). Such a scenario would render the problem of studying optimal power trivial since power would be unbounded and independent of evolution of the system with time. If, on the other hand, the process is required to be cyclic one must have $H \rightarrow H' \rightarrow H$. For a sudden quench, Equation (3.6) then vanishes in the numerator⁶.

Requiring cyclicity is here the same as demanding that energies be measured with respect to the same reference Hamiltonian at the beginning and at the end of the protocol⁷. Any evolution can be made cyclic by adding a sudden quench at the end, which returns the driving Hamiltonian back to the original reference Hamiltonian, leaving the system state unaffected in the process. In Equation (2.1), which expressed

⁶For a perfectly sudden quench, Equation (3.6) also vanishes in the denominator. Every physical process will of course take some amount of time T by definition – even if T can become arbitrarily small. It hence speaks to physical intuition that P does in fact vanish in realistic cases. Pathological examples, however, where P remains finite for $T \rightarrow 0^+$, could be contrived. A more precise statement about how such pathological cases can be avoided in the asymptotic limit $T \rightarrow 0^+$ follows in the context of Section 3.4.

⁷This is captured by the difference between *inclusive* and *exclusive* work that can be found in the literature [Jarzynski, 2007; Campisi et al., 2011]. In this chapter when we speak of *work* we mean *exclusive work*.

the driving Hamiltonian of a cyclic process as $K(t) = H + V(t)$, one would in this spirit formally allow for $V(T) \neq 0$ and then add a quench $V(T) \rightarrow 0$ at the end of the protocol.

This establishes a notion of power in quantum evolution. In practice, both power and work output of a mechanical device are of interest: a powerful process is of little use if it only does a vanishing amount of work. Similarly, a process that is capable of generating a large amount of work is only useful if it can do so within a reasonable time-frame. When optimising a mechanical or thermodynamic process, it is hence often desirable to do so with respect to a target function that reflects optimisation for both – work and power – at the same time. We introduce the family of target functions

$$\mathcal{F} := P^\alpha W^{1-\alpha} = \frac{W}{T^\alpha}, \quad (3.7)$$

where the process duration T is a free variable (cf. Equation (3.6)) and will generally be part of an optimal solution. $\alpha : 0 \leq \alpha \leq 1$ remains a free parameter. For the extremal case of $\alpha = 1$ the expression for power is recovered. Optimisation for $\alpha = 0$, on the other hand, recovers the expression for ergotropy as derived by Allahverdyan et al. [2004].

3.3 Quantum speed limits and constrained driving

At this point, one may wonder if there any physical limits at all to maximising Equation (3.7):

Even if the maximal work is finite, cannot the process duration in the denominator of Equation (3.7) be reduced to arbitrarily small values?

The quantum speed limits, summarised in Box 3.1, give an intuition that this is in fact not so: reducing the duration of a quantum process, which takes a state ρ to a

different state ρ' , generally comes at the cost of increasing both the available mean driving energy as well as its variance [Deffner and Lutz, 2013a].

Box 3.1: Quantum speed limits

The oldest quantum speed limit (QSL) was introduced by Mandelstam and Tamm [1945]^a. Cast into up-to-date notation [Uffink, 1993], it bounds the evolution time T from a state ρ to a unitarily connected state ρ' by the product of their distance (given by the Bures Angle, cf. Box 3.2) and the inverse of $\Delta H = \sqrt{\langle H^2 \rangle - \langle H \rangle^2}$, the energy uncertainty in the (time-independent) system Hamiltonian H :

$$T \geq \hbar \mathcal{L}(\rho, \rho') \frac{1}{\Delta H}. \quad (3.8)$$

A second and independent QSL was later discovered by Margolus and Levitin [1998]. Originally formulated for pure states, it bounds the time $T_\perp$ necessary to evolve from a state $|\psi\rangle$ to an orthogonal state $|\psi_\perp\rangle$ by the inverse of the energy expectation value with respect to the ground state energy ϵ_0 of a time-independent system Hamiltonian H :

$$T_\perp \geq \hbar \frac{\pi}{2} \frac{1}{\langle H \rangle - \epsilon_0} \quad (3.9)$$

In their original formulations only applicable to time-independent driving, the speed limits have since been extended to more general statements [Giovannetti et al., 2003], including the possibility of time-dependent unitary driving [Deffner and Lutz, 2013a] as well as non-unitary evolution [Taddei et al., 2013; Deffner and Lutz, 2013b; del Campo et al., 2013; Uzdin et al., 2012; Pires et al., 2015]. For the present purposes, only speed limits for unitary evolution are of relevance. In this case, the Mandelstam-Tamm (MT)- and Margolus-Levitin (ML)-type speed limits can be stated in a single inequality-bound for the time T

taken to evolve from a state ρ to some other (unitarily connected) state ρ' :

$$T \geq T_{QSL} := \hbar \mathcal{L}(\rho, \rho') \max \left\{ \frac{1}{\Delta E_T}, \frac{1}{E_T} \right\}. \quad (3.10)$$

The evolution happens under unitary dynamics governed by the time-dependent Hamiltonian $K(t)$. In specifying the limits determined by Equation (3.10), we have used the following averages

$$\Delta E_T := \frac{1}{T} \int_0^T dt \sqrt{\langle K(t)^2 \rangle - \langle K(t) \rangle^2}, \text{ and} \quad (3.11)$$

$$E_T := \frac{1}{T} \int_0^T dt [|\text{tr}[\rho(0)K(t)]| - \kappa_0(t)]. \quad (3.12)$$

Here, ΔE_T is the time-averaged variance of the energy with respect to the state $\rho(t)$ at time t during the evolution (with $\langle X \rangle \equiv \text{tr}[\rho(t)X]$). E_T , on the other hand, is the time-averaged expectation value of the energy with respect to $\rho(0)$, defined in relation to the instantaneous groundstate energy $\kappa_0(t)$ of the driving Hamiltonian $K(t)$.

Remarks

- (a) If the ML bound is satisfied, any evolution along a geodesic defined by the Fubini-Study metric (Box 3.2) guarantees that the MT bound is saturated.
- (b) The step from Equations (3.8) and (3.9) to Equation (3.10) is far from trivial because the bounds obtain a very different interpretation under time-dependent driving. In the original, time-independent case, ΔH and H are characteristics of an isolated system. We may think of a piston which is stationary in a fixed position. Even though the system is thermo-

dynamically out-of equilibrium, corresponding equilibrium variables like volume and pressure are fixed and the (reversible) system dynamics are completely specified by the original system state. Once time-dependence is included in $K(t)$, however, the bounds that Equation (3.10) imposes do not characterise the system itself any more but rather its driving. In the piston analogy, the evolution is now determined not only by the state of the medium inside the piston's cavity but moreover and crucially by the mechanism that drives the piston, and, importantly, the constraints on that driving. This reflects the notational difference between H and $K(t)$ in this thesis.

- (c) Equation (3.10) is circular: T appears on both sides of the inequality. Moreover, in the general case, knowledge of the full evolution $\rho(t)$ is necessary in order to calculate a lower bound on its duration. However:
- (d) Given an initial state $\rho(0)$ and a driving Hamiltonian $K(t)$, the state's unitary evolution is fully specified by the time-dependent Schrödinger equation and entirely deterministic. If $\rho(t)$ and ρ' ever equate during the evolution this will happen after some fixed time T_1 for the first time. T_1 is completely determined by the initial conditions.
- (e) Due to its dependence on $\hbar$, it is apparent that the quantum speed limits are indeed truly quantum. In the quantum-to-classical limit $\hbar \rightarrow 0$ the lower bound on the evolution time vanishes.

The explicit notation in this box serves to highlight this point. Everywhere else in this thesis, the convention $\hbar = 1$ continues to hold.

- (f) There is a close connection between quantum speed limits and the so-called *quantum brachistochrone* [Carlini et al., 2006]. The latter asks

for the fastest driving that takes a given (i.e., pure) input state $|\psi\rangle$ to a desired output state $|\phi\rangle$ allowing for a set of external constraints. If the only external constraint is a bound on the energy variance, the MT limit is recovered. The corresponding solution to the quantum brachistochrone problem hence saturates this bound in absence of further constraints [Carlini et al., 2006].

The question of finding time-optimal realisations of desired unitary operations has been posed in a similar spirit [Carlini et al., 2007].

^aIn the same paper, the so-called *energy-time uncertainty relation* was derived on the same grounds as the QSL: $\Delta H \Delta T \geq \frac{\hbar}{2}$. Here, ΔT is the minimum time necessary to change the expectation value of an observable by an amount that equals its uncertainty. Calling this relationship an uncertainty relation, however, may lead to misunderstandings: since no time-operator exists in quantum mechanics ΔT does not correspond to the variance associated with an observable. The Mandelstam-Tamm QSL is hence of a rather different nature than other uncertainty principles.

Box 3.2: Metrics and distances in state space

Quantum state space (projective Hilbert space) is endowed with a metric called *Bures metric*, which in turn defines a distance called *Bures Angle*^a [Bengtsson and Życzkowski, 2006]

$$\mathcal{L}(\rho, \sigma) := \arccos \left[\sqrt{F(\rho, \sigma)} \right], \text{ where} \quad (3.13)$$

$$\sqrt{F(\rho, \sigma)} := \text{tr} \sqrt{\sqrt{\rho} \sigma \sqrt{\rho}} \quad (3.14)$$

is the *root fidelity* [Uhlmann, 1976; Jozsa, 1994]. A distance is naturally implied by a metric as the corresponding length of a shortest path between two states – a *geodesic*.

In the case of pure states, the Bures angle simplifies to the better-known *Fubini-Study distance*

$$D(|\psi\rangle, |\phi\rangle) := \arccos |\langle \psi | \phi \rangle|, \quad (3.15)$$

and the fidelity simplifies to $F(|\psi\rangle, |\phi\rangle) = |\langle\psi|\phi\rangle|^2$.

The *Fubini-Study metric*, which applies to pure states and can be stated explicitly by expressing the square line element

$$ds^2 = \frac{\langle d\psi | d\psi \rangle}{\langle \psi | \psi \rangle} - \frac{\langle d\psi | \psi \rangle \langle \psi | d\psi \rangle}{\langle \psi | \psi \rangle^2}. \quad (3.16)$$

^aTerminology can be a bit confusing here: there exists another distance referred to as either *Bures distance* or *Bures length*. It is related to but not the same as the Bures angle which is used here. The term *fidelity* is similarly ambiguous as some authors prefer to call *fidelity* what is the *root fidelity* $\sqrt{F}$ in our case.

As highlighted in Box 3.1, the speed limits (Equation (3.10)) are not prescriptive for determining optimal driving because they depend on the the system state at each instant in time. Approaches to the quantum brachistochrone problem, on the other hand, would be suitable for finding optimal evolution under external constraints. Both the quantum speed limits and the quantum brachistochrone apply to problems with a target output state. In the present context, however, the target state is not of relevance but rather the output average energy. The latter could be the same for different target states, and vice versa: different output states with the same energy are generally located at different distances in state space from a given input state.

Alternative bounds to the quantum speed limit have been developed which depend on norms of the driving Hamiltonian [Uzdin et al., 2012]. They are closest in spirit to the approach presented in this chapter. At any rate, the speed limits serve us well in establishing an intuition for the necessity of a external constraints on the driving. We return to the relation between the present results on powerful unitary driving and the bounds imposed by quantum speed limits in Section 3.6.

Based on the discussion in this section, it is clear that bounds on the driving Hamiltonian are natural constraints that must be incorporated into the analysis of quantum batteries operating in finite time. In the following sections, bounds are

introduced which acknowledge such external constraints on the driving. They are external in the sense that they depend on the driving Hamiltonian alone but not the system state. In particular, the largest energy gap of the driving Hamiltonian will be restricted by the value E_{max} . This corresponds to restricting the maximal energy available for external driving⁸. In the following section, we optimise such driving for power in a simple, paradigmatic context.

3.4 Powerful wit charging

Narrowing the focus to a single qubit, in this section, we analytically derive optimally powerful driving with respect to the target function, Equation (3.7). Without loss of generality, we take the reference Hamiltonian to be $H = |1\rangle\langle 1|$. A qubit endowed with such a non-degenerate reference Hamiltonian is called a *wit* – short for *work qubit*. Here, the Hamiltonian establishes a unit of energy – the equivalent of a pure wit’s capacity. All energies in this chapter may hence be thought of as being given in terms of single wit energies.

To begin the derivation, we parametrise the driving Hamiltonian $K(t)$ with control functions $k^x(t)$, $k^y(t)$, and $k^z(t)$ for the Pauli operators σ_x, σ_y , and σ_z . These three control functions can be grouped in a vector $\mathbf{k}(t) := (k^x(t), k^y(t), k^z(t))^T$ – and similarly for the Pauli operators $\boldsymbol{\sigma} := (\sigma_x, \sigma_y, \sigma_z)^T$. Here, the exponent T indicates transposition. The instantaneous eigenvalues of

$$K(t) := \mathbf{k}(t) \cdot \boldsymbol{\sigma} \text{ are} \tag{3.17}$$

$$\kappa(t)^\pm = \pm |\mathbf{k}(t)| = \pm \sqrt{\sum_j (k^j(t))^2}. \tag{3.18}$$

⁸The external bound on the driving is further discussed in Section 3.5 where the Schatten p -norms are introduced (Box 3.3). For now, all external constraints that we use effectively impose upper bounds the operator norm of the driving Hamiltonian shifted by its ground state.

In order to achieve a thermodynamically sensible constraint, we bound the difference between the instantaneous eigenvalues by a maximum, externally given value E_{max} :

$$\kappa^+(t) - \kappa^-(t) = 2\sqrt{\sum (k^j(t))^2} \leq E_{max}t \quad \forall t. \quad (3.19)$$

This corresponds to restricting the p -norms of the driving Hamiltonian shifted by its ground state energy (cf. Box 3.3).

The following derivation is informed by recent results, where a full solution of general time-optimal control of qubit operations was derived for the first time [Hegerfeldt, 2013, 2014]. Similarly, time-optimal driving is related to the so-called *quantum brachistochrone* problem (cf. Box 3.1). Both of these approaches, however – as noted above – differ from the present analysis in the sense that they are concerned with a process which takes some input state ρ to a specific target state ρ' . Conversely, the present interest lies on the average work done in a driving process rather than the output state. While the qubit state's purity has to be conserved during the evolution as a consequence of unitarity, it makes no difference what relative phase the output state has. That is, in the Bloch sphere picture, only the state's z coordinate is of interest. In this context, ρ can be any qubit state (active or passive), i.e., parametrised by angles θ and ϕ , and a radius r which remains constant during evolution. The value of ϕ at the beginning or the end of the evolution has no bearing on the result. As we will see below, this leads to zero driving along σ_z in the optimal case.

In order to optimise the power, we invoke the von Neumann equation for the state's unitary evolution:

$$i\frac{d}{dt}\rho(t) = [K(t), \rho(t)] = \frac{1}{2}[\mathbf{k}(t) \cdot \boldsymbol{\sigma}, \mathbf{I} + \mathbf{a}(t) \cdot \boldsymbol{\sigma}], \quad (3.20)$$

where $\rho(t) = \frac{1}{2}(\mathbf{I} + \mathbf{a}(t) \cdot \boldsymbol{\sigma})$ is parametrised by its Cartesian decomposition $\mathbf{a}(t)$ in terms of Pauli operators, i.e.,

$$\mathbf{a}(t) = (a^x(t), a^y(t), a^z(t))^T = r(\sin \theta(t) \cos \phi(t), \sin \theta(t) \sin \phi(t), \cos \theta(t))^T. \quad (3.21)$$

With Einstein summation convention and using the Levi-Civita symbol, the evolution becomes

$$\frac{d}{dt}\rho(t) = k^l(t)a^m(t)\epsilon_{lmn}\sigma_n. \quad (3.22)$$

The goal is to achieve maximum average power $P = W/T$ (or indeed $\mathcal{F} = W/T^\alpha$) over the duration T of the whole process. To reflect cyclicity, as before, exclusive work (and consequently: power) defined with respect to the initial Hamiltonian H is considered: charging increases the energy in the state $\rho(t)$ with respect to the time-independent reference H . Optimality is hence achieved by first optimising $\frac{d}{dt}\text{tr}[\rho(t)H]$ at each instant in time over the driving $\mathbf{k}(t)$ and then finding the optimal process duration T . Using Equation 3.22 we obtain

$$\text{tr} \left(\frac{d}{dt}\rho(t)H \right) = k^y(t)a^x(t) - k^x(t)a^y(t) \quad (3.23)$$

$$= (k^y(t) \cos \phi(t) - k^x(t) \sin \phi(t))r \sin \theta(t). \quad (3.24)$$

The optimal protocol under the above constraint is hence found for

$$\mathbf{k}(t) = \frac{1}{2}E_{max}(-\sin \phi(t), \cos \phi(t), 0)^T. \quad (3.25)$$

This implies that in the optimal case no driving happens in the direction of the reference Hamiltonian. The solution corresponds to driving along the geodesic with

fixed r and $\phi(t) = \phi_0$, at constant angular speed E_{max} – that is

$$\theta(t) = \theta_0 + \frac{1}{2}E_{max}t. \quad (3.26)$$

For a fixed input state, the goal is now to optimise the average power, or more generally the function $\mathcal{F}^9$:

$$\mathcal{F} = \frac{W}{T^\alpha} = \frac{\text{tr}[H\rho'] - \text{tr}[H\rho]}{T^\alpha} \quad (3.27)$$

$$= \left(\frac{E_{max}}{2(\theta_T - \theta_0)} \right)^\alpha r \left(\frac{\cos \theta_0}{2} - \frac{\cos \theta_T}{2} \right) \quad (3.28)$$

$$= \frac{r}{2T^\alpha} [\cos \theta_0 - \cos(\theta_0 + \frac{1}{2}E_{max}T)]. \quad (3.29)$$

Linearity of the driving time in θ_T (cf. Equation 3.26) permits the choice of either variable for optimisation. The optimal solution is found for the driving time T_m that satisfies:

$$\cos(\theta_0 + \frac{1}{2}E_{max}T_m) - \frac{E_{max}T_m}{2\alpha} \sin(\theta_0 + \frac{1}{2}E_{max}T_m) = \cos \theta_0. \quad (3.30)$$

This equation can be understood geometrically by rewriting it as

$$\Delta z_T = \frac{E_{max}T}{2\alpha} p_T^{xy}, \quad (3.31)$$

which is fulfilled when the qubit has travelled a vertical distance Δz_T on the Bloch sphere which equals the length of its state's projection onto the x - y -plane, p_T^{xy} , weighed by a factor $\frac{1}{2\alpha}E_{max}T$.

⁹For a given input state, Equation 3.26 already offers an answer to two related questions: what is the maximum work that can be achieved in time T ? What is the minimum time necessary to achieve work W (parametrised by θ)?

The solution for $\mathcal{F}$ has a non-trivial maximum which occurs after different driving times t for different α as is illustrated for an example in Figure 3.1. The cone of optimal output states for initially thermal states is pictured on the Bloch sphere in Figure 3.2. We point out that for certain initial conditions it is possible to achieve finite power at time $T \rightarrow 0^+$. This can be regarded as pathological and it is worth pointing out that for $\alpha < 1$ and $\theta_0 < \pi$ the optimum is always reached for finite T_m .

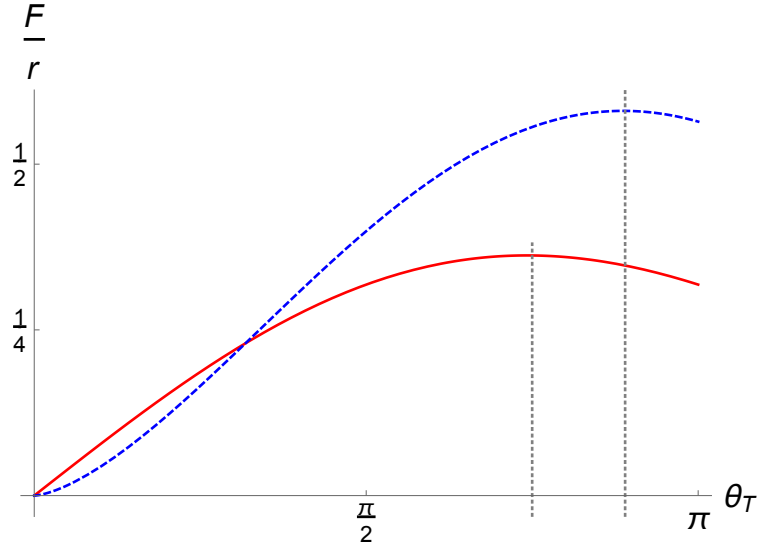


Figure 3.1: Target function $\mathcal{F}$ in units of r^{-1} for $\alpha = 1$ [red, solid] and $\alpha = \frac{1}{2}$ [blue, dashed]. Taking the generic, thermal input state $\tau_\beta = \frac{1}{2}[(1+r)|0\rangle\langle 0| + (1-r)|1\rangle\langle 1|]$ with $r := \frac{1-\exp[-\beta]}{1+\exp[-\beta]}$, power $P = \frac{W}{T}$ (i.e., $\alpha = 1$), and $\sqrt{P\bar{W}}$ (i.e., $\alpha = \frac{1}{2}$) are plotted against $\theta_T = \frac{1}{2}E_{max}T$. Maximal power is reached for $\theta_T \approx 0.74\pi$; $\sqrt{P\bar{W}}$ is maximal at $\theta_T \approx 0.89\pi$ [grey, dotted lines].

In summary, the result of this section is an optimal protocol for achieving maximal $\mathcal{F}$ (e.g. power) for any given input wit state ρ , reference Hamiltonian H , external constraint E_{max} , and suitable choice of α . The optimal protocol is specified by Equations (3.25) and (3.30).

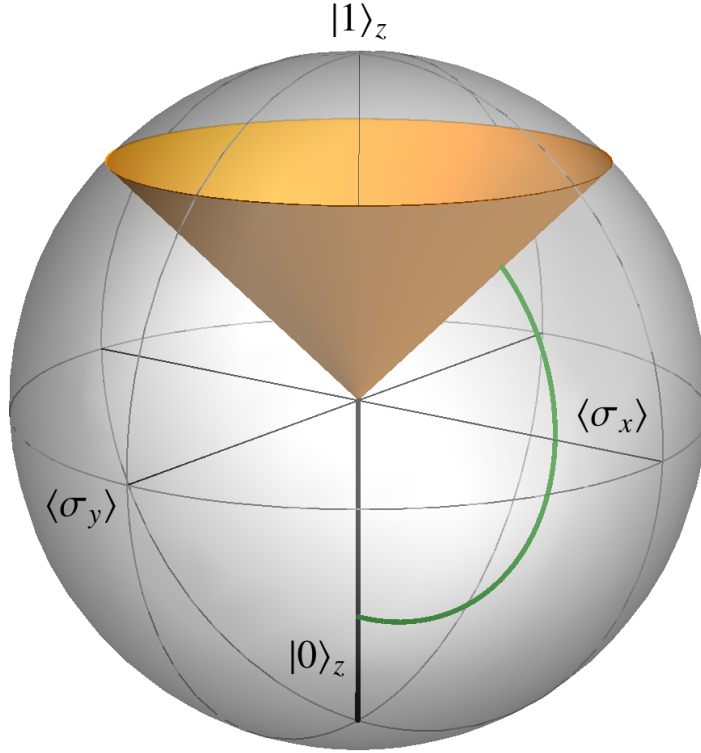


Figure 3.2: Path through Bloch sphere. For a battery in an initially thermal state (i.e., $\tau_\beta = \frac{1}{2}[(1+r)|0\rangle\langle 0| + (1-r)|1\rangle\langle 1|]$ with $r := \frac{1-\exp[-\beta]}{1+\exp[-\beta]}$, thick black line), and $E_{max} = 1$, this graph shows the cone of states that achieve maximum average power on the Bloch sphere. Maximal power is reached for $\theta_T \approx 0.74\pi$. Note that a cone only appears for initial thermal states. For any other state, ϕ is fixed and the optimal output state lies on a ray at $\phi_T = \phi_0$. The green line depicts an exemplary trajectory for $r = \frac{2}{3}$ and $\phi = 0$.

3.5 Power advantage due to entanglement

Having found the maximally powerful evolution of a single qubit, we now proceed by looking at larger systems, in particular arrays of N wits – i.e., $\rho^{(N)} = \rho^{\otimes N}$ as illustrated in Figure 3.3. The aim of this section is to demonstrate that when global, entangling operations are allowed on the array (rather than local, parallel operations for each wit), an increase in power per wit linear in N can be achieved.

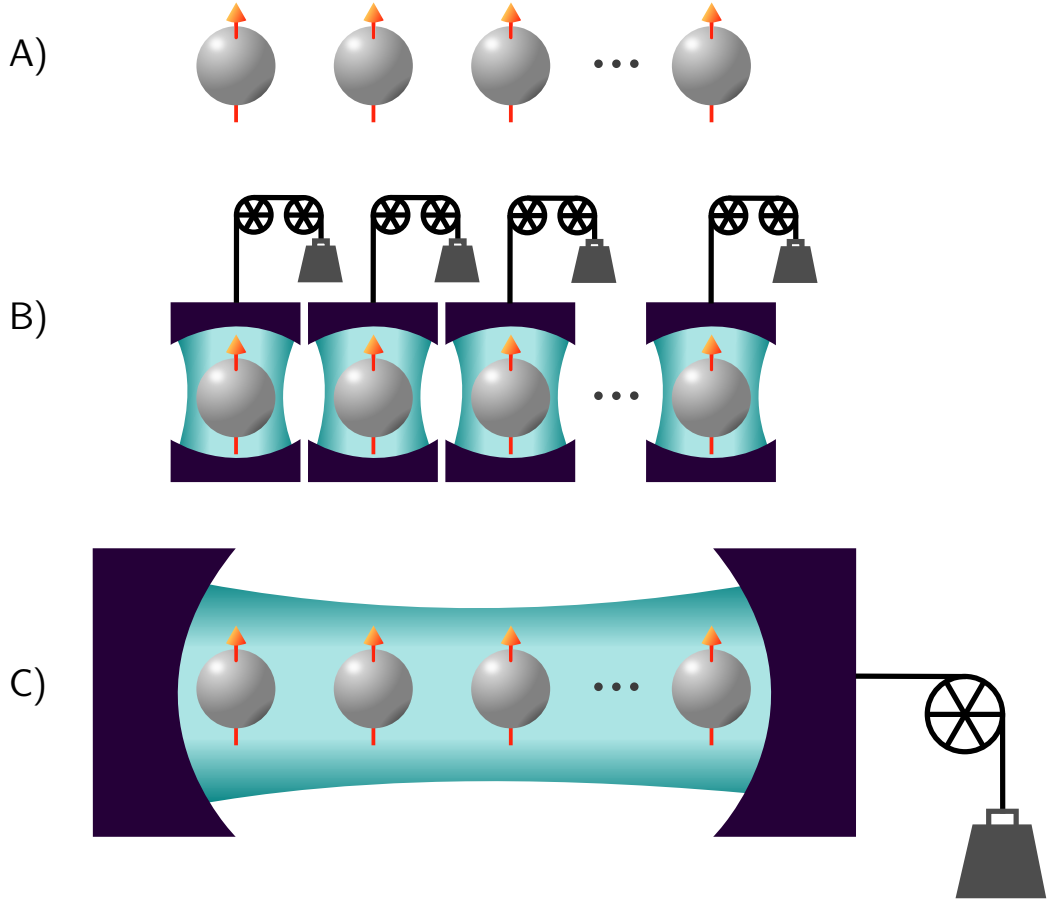


Figure 3.3: An array of wits (A) can either be driven in parallel (B), for instance as prescribed by Equation (3.33), or globally (C), i.e., as given by Equation (3.35).

Regardless of the driving, the reference Hamiltonian $H^{(N)}$ is the sum of the local Hamiltonians from the single wit case

$$H^{(N)} := \sum_k |1\rangle_k \langle 1|_k \bigotimes_{j \neq k} \mathbf{I}^{(j)}, \quad (3.32)$$

where j and k label the wits. For now, we do not want to decrease the purity of the local states (with cyclic operation in mind). This condition – that there is no reduction in the purity of the reduced states at the end of the protocol – is called condition of *no degradation*. It implies that the output state has to be separable. Restricting the analysis to pure states for now, we are interested in going from $|0\rangle^{\otimes N}$ to $(a|0\rangle + b|1\rangle)^{\otimes N}$. Since a full optimisation over all possible unitary transformations

is not analytically feasible we will content ourselves with finding a specific evolution that shows an improvement in power per qubit compared to the single qubit case.

In particular, let us consider full charging such that $|0\rangle^{\otimes N} \rightarrow |1\rangle^{\otimes N}$. For parallel driving, e.g. Equation (3.25), labelled by $\mathcal{P}$, the (time-independent) driving Hamiltonian in the interval $0 \leq t \leq T$ is

$$K_{\mathcal{P}}^{(N)} = \frac{1}{2} \sum_k^N E_{max} (\cos \phi_0 \sigma_y^{(k)} - \sin \phi_0 \sigma_x^{(k)}) \bigotimes_{j \neq k}^N \mathbf{I}^{(j)}, \quad (3.33)$$

where the angle ϕ_0 can be set to $\frac{3}{2}\pi$ without loss of generality. This Hamiltonian possesses $N + 1$ equidistant eigenvalues, with the gap between the largest and the lowest eigenvalue given by NE_{max} . In order to allow for a fair comparison, we will hence equally allow for a maximum energy gap of $E_{max}^{(N)} = NE_{max}$ in the case of global driving. The work done is trivially $W = N$: the average work per qubit is unity. The driving time is $T_{\mathcal{P}} = 2\pi/E_{max}$ – trivially the same as in the single wit case. Equally, the power per wit for parallel driving is the same as for a single wit (by construction):

$$\frac{P_{\mathcal{P}}}{N} = \frac{E_{max}}{2\pi}. \quad (3.34)$$

Global (and entangling) driving, indicated by $\mathcal{G}$, is achieved by evolution with¹⁰

$$K_{\mathcal{G}}^{(N)} = \frac{1}{2} E_{max}^{(N)} \sigma_x^{(N)} := \frac{1}{2} E_{max}^{(N)} \left(|1\rangle^{\otimes N} \langle 0|^{\otimes N} + |0\rangle^{\otimes N} \langle 1|^{\otimes N} \right) \quad (3.35)$$

for a duration $T_{\mathcal{G}} = 2\pi/E_{max}^{(N)}$. The average work in this process is again $W = N$.

The average power consequently reads

$$P_{\mathcal{G}} = \frac{E_{max}^{(N)}}{2\pi} N \quad (3.36)$$

¹⁰This global driving is in fact optimal for the current scenario. Generally, in absence of further constraints, driving between two given states $|a\rangle$ and $|b\rangle$ is optimised by evolution with a Hamiltonian $K \propto |a\rangle\langle b| + |b\rangle\langle a|$.

and depends on the driving constraint $E_{max}^{(N)}$. Permitting for the same constraint as in the parallel case – that is $E_{max}^{(N)} = N E_{max}$ – an N -fold increase in power per qubit is achieved:

$$\frac{P_{\mathcal{G}}}{N} = N \frac{E_{max}}{2\pi} = N \frac{P_{\mathcal{P}}}{N}. \quad (3.37)$$

Interestingly, this advantage due to correlations (or, in other words, due to the non-local character of $K_{\mathcal{G}}$) appears even though initial and final states are separable. A geometric explanation will be provided in Section 3.6.

Extension to initially thermal array states

Based on the intuition gained from the pure state example, we now consider an extension to the more general scenario where the battery array starts in a thermal state $\tau_{\beta}^{(N)} := \tau_{\beta}^{\otimes N}$.

This subsection is slightly more technical than the rest of this chapter. It serves the purpose of generalising the results presented so far from pure states to thermal states. We proceed in three steps:

- 1) First, we express the thermal state of the N -qubit array (Equation (3.39))
- 2) Then, we introduce Schatten p -norms (Box 3.3) and consider carefully the bounds which the driving Hamiltonians have to fulfil.
- 3) Finally, we propose a specific driving $K_{\mathcal{T}}^{(N)}$ (Equation (3.44)) and demonstrate that it leads to the same enhancement in power per qubit if we compare global driving of the initially thermal array to local driving (Equation (3.51)).

As highlighted in Section 2.1.1 and Appendix A, the combination of identical thermal states results in a global thermal state at the same temperature and vice-versa: the subsystems of a globally thermal state are themselves thermal at the same temperature (in absence of interactions). For the specific case of wits, all passive

states are in fact thermal, as pointed out above:

$$\tau_\beta = \frac{1}{2}[(1+r)|0\rangle\langle 0| + (1-r)|1\rangle\langle 1|], \quad (3.38)$$

with spherical coordinates $r = \frac{1-\exp[-\beta]}{1+\exp[-\beta]}$ and $\theta = \pi$; the value of ϕ is arbitrary. The global, N -qubit state $\tau_\beta^{(N)} := \tau_\beta^{\otimes N}$, a special case of Equation (A.9), is also thermal:

$$\tau_\beta^{(N)} = \frac{1}{(1+e^{-\beta})^N} \sum_{m=0}^N e^{-\beta E_m} \sum_{\mu_m} |E_m, \mu_m\rangle\langle E_m, \mu_m|, \quad (3.39)$$

with corresponding energies $E_m = m$ and degeneracies labelled by μ_m . Full charging will lead to a complete inversion of populations, yielding the maximally active state $\omega_\beta^{(N)}$. In this particular case – due to the degenerate nature of the gaps in the global Hamiltonian’s spectrum – $\omega_\beta^{(N)}$ has Gibbs-distributed populations with negative temperature $-\beta$, i.e., $\omega_\beta^{(N)} = \tau_{-\beta}^{(N)}$. The work resulting from a full charge is

$$W = \text{tr} \left[\left(\omega_\beta^{(N)} - \tau_{-\beta}^{(N)} \right) H^{(N)} \right] = N \tanh \frac{\beta}{2}. \quad (3.40)$$

We now demonstrate that the same speedup as before can be obtained even if the N wits on the array start in a thermal state. Again, we show this for separable input and output states, and full charging.

First, however, the *Schatten p -norms* are introduced in Box 3.3 in order to facilitate the specifications of external bounds on the driving.

Box 3.3: Schatten p -norms

For $p \geq 1$ the (Schatten) p -norms of a Hermitian operator $A := \sum a_k |a_k\rangle\langle a_k|$ are given by [Horn and Johnson, 2013]:

$$\|A\|_p := \left(\sum_k |a_k|^{\frac{1}{p}} \right)^p, \text{ with the limiting case} \quad (3.41)$$

$$\|A\|_\infty := \max_k |a_k|. \quad (3.42)$$

$\|\cdot\|_1$ is called *trace norm*, $\|\cdot\|_2$ is the *Frobenius norm*. The *operator norm* is given by $\|\cdot\|_\infty$ and simply expressed as $\|\cdot\|$ in this thesis.

Gauge transforming a Hamiltonian by adding a constant (for instance, the ground state energy) has no perceptible physical effect. The norms, however, are not invariant under such a gauge transformation. A sensible choice of gauge (which was implicitly made above) is to apply the norms to $K(t) - \kappa_0(t)\mathbf{I}$ where $\kappa_0(t)$ is the instantaneous ground state energy of the driving Hamiltonian. Taking this gauge choice into account in the single wit case, all p -norms are in fact the same:

$$\|K(t) - \kappa_0(t)\|_p = \kappa_+(t) - \kappa_-(t) \quad \forall p. \quad (3.43)$$

The same holds for the pure array example where the driving Hamiltonian only has two non-zero eigenvalues. In the case of a larger dimensional effective Hilbert space (as in this section), however, the norms differ for different p .

Up until now, we have implicitly bounded the driving Hamiltonians $K(t)$, $K_{\mathcal{P}}^{(N)}$, and $K_{\mathcal{G}}^{(N)}$ by their operator norms. We continue to use the operator norm as a norm of choice but retain the realisation that the results may be contingent on this choice. We return to the possibility of using an alternative p -norm for defining the bounds below.

In the case of the pure array, the operator norm of the parallel driving Hamiltonian was computed first and then applied to bound the choice of the entangling operation used for the demonstrated speedup. The same approach will be taken in this section.

We propose to drive the initially thermal array with the natural generalisation of Equation (3.35):

$$K_{\mathcal{T}}^{(N)} = \frac{1}{2} \sum_j^{N^*} \lambda_j^{(N)} \sigma_x^{(N,j)}, \quad (3.44)$$

where $N^* = \frac{N}{2} - 1$ for even N and $N^* = \frac{N-1}{2}$ for odd N . If the additional term $\lambda_{\frac{N}{2}}^{(N)} \left| \frac{N}{2} \right\rangle \left\langle \frac{N}{2} \right|$ is added to $K_{\mathcal{T}}^{(N)}$ in the case of even N , the driving is full rank in both cases (even and odd). The prefactors $\lambda_j^{(N)}$ are yet to be determined, in compliance with suitable bounds. The operators $\sigma_x^{(N,j)}$ connect subspaces of energy j to those of energy $N - j$:

$$\sigma_x^{(N,j)} := \sum_{\nu_j} (|j, \nu_j\rangle \langle N - j, \nu_j| + |N - j, \nu_j\rangle \langle j, \nu_j|), \quad (3.45)$$

where $|j, \nu_j\rangle$ is an eigenstate of $H^{(N)}$ with energy j . ν_j labels the $\binom{N}{j}$ degenerate states within the j th eigenenergy subspace. If we consider each of the subspaces connected by $\sigma_x^{(N,j)}$ separately, it becomes apparent that the smallest $\lambda_j^{(N)}$ dictates the time for a full charge – with the evolution operator

$$U_{\mathcal{T}} = \exp[-iK_{\mathcal{T}}^{(N)}T]. \quad (3.46)$$

Consequently, since the final state is required to be separable, all prefactors $\lambda_j^{(N)}$ are set to be the same: $\lambda_j^{(N)} = \lambda^{(N)} \forall j$. Their magnitude equates the operator norm to which the bound will apply and determines the fastest duration of a full charging process:

$$T = \frac{2\pi}{\lambda^{(N)}}. \quad (3.47)$$

In order to find legitimate bounds on $K_{\mathcal{T}}^{(N)}$, and hence, $\lambda^{(N)}$, a comparison to parallel driving is again instructive. The parallel driving Hamiltonian $K_{\mathcal{P}}^{(N)}$, defined by (Equation (3.33)), has eigenvalues

$$\kappa_k^{(N)} = E_{max} \left(k - \frac{N}{2} \right), \text{ with } 0 \leq k \leq N. \quad (3.48)$$

The operator norm of $K_{\mathcal{P}}^{(N)}$ shifted by the ground state energy is accordingly computed to be

$$\|K_{\mathcal{P}}^{(N)} - \kappa_0^{(N)}\|_{\infty} = NE_{max}. \quad (3.49)$$

This norm now implies the desired bound on the prefactors $\lambda^{(N)}$ which appear in the driving $K_{\mathcal{T}}^{(N)}$:

$$\lambda^{(N)} \leq NE_{max}. \quad (3.50)$$

Cosequently, like in the previously considered pure case, the optimal power per wit, $P_{\mathcal{T}}/N$, compared to the parallel case, scales linearly with N :

$$\frac{P_{\mathcal{T}}}{N} = N \frac{E_{max}}{2\pi} \tanh \frac{\beta}{2} = N \frac{P_{\mathcal{PT}}}{N} \quad (3.51)$$

Here, we have used Equation (3.40) to express the work, and Equation (3.47) with Equation (3.50) to express the process duration of the global driving. The duration of the parallel driving is the same as before and only the work has changed in that case (cf. Equation (3.40)), yielding the total power $P_{\mathcal{PT}}$ for driving the thermal array wits in parallel.

It is worth pointing out that if, following the same analysis, either the trace norm or the Frobenius norm are used instead of the operator norm the leading order scaling of the power per wit remains linear in N , albeit not directly proportional.

This concludes the demonstration that if an array of N wits is charged globally an increase in power per wit, linear in N , can be achieved with entangling operations compared to separable evolution. This holds even if initial and final state are required to be separable as was demonstrated by example. Remembering that all passive wit states are in fact thermal, this result applies to all initial wit array states from which no work can be locally extracted in a cyclic unitary process – that is, all arrays of fully discharged wit batteries according to the definition presented at the beginning of this chapter.

One may furthermore recognise that even the pure state case already represents a more general description than may be apparent at first sight. This is due to the fact that, while thermal excitations play a role in some popular implementations of qubits, they are in fact negligible in those systems which lend themselves as promising candidates for the implementation of quantum batteries. Such systems, for instance optical qubits in ions, are characterised by energy gaps which leave thermal populations negligibly small even at room temperature – leave alone temperatures commonly encountered in experiments. When discussing the results of this chapter in the following section, we hence return to considering the pure state example for the sake of simplicity and clarity.

3.6 Discussion

We now provide an intuitive explanation of the results, in particular of the speedup observed in the previous section. We also briefly consider implementability of the

driving Hamiltonians that were proposed for entangling driving before concluding in the following section.

3.6.1 Geometric interpretation and comparison to speed limits

What has been demonstrated in the previous section is that, if a time $T_{\mathcal{P}}$ is required to fully charge N pure wits in parallel (i.e., $|0\rangle^{\otimes N} \rightarrow |1\rangle^{\otimes N}$), the same task can be performed in a time $T_{\mathcal{G}} = \frac{1}{N}T_{\mathcal{P}}$ if entangling operations are permitted. The aim of this section is to provide some intuition for this speedup. We proceed in two steps. First, we demonstrate that the path length of the evolution in projective Hilbert space is $\sqrt{N}$ -times longer in the parallel case compared to the entangling case. A second factor of $\sqrt{N}$ is ‘hidden’ in the speed limits which can be invoked to understand the scaling of the evolution time with the path length.

In order to calculate and compare the path length in state space between the global and local pure state case (i.e., $|0\rangle^{\otimes N} \rightarrow |1\rangle^{\otimes N}$), we first note that in the global case the proposed evolution does in fact prescribe a path along a geodesic. Consequently, the path length is directly given by the Bures angle $\mathcal{L}$ between the input and the output state. For pure states, the Bures angle is equal to the Fubini-Study distance and we directly see (cf. Box 3.2):

$$\mathcal{L}\left(|0\rangle^{\otimes N}, |1\rangle^{\otimes N}\right) = \arccos\left|\langle 0|^{\otimes N} |1\rangle^{\otimes N}\right| = \frac{\pi}{2} \quad (3.52)$$

The same equality holds for the single wit case (with $|0\rangle^{\otimes N}$ and $|1\rangle^{\otimes N}$ replaced by $|0\rangle$ and $|1\rangle$).

In the case of parallel driving, we note that the square of the line element is additive under tensor product. That is, for $|\psi_{\mathcal{P}}\rangle = \otimes_j |\psi_j\rangle$, $ds_{\mathcal{P}}^2 = \sum_j ds_j^2$ ($\mathcal{P}$ again indicates the parallel, global quantities). This can be seen as follows. The line element of the Fubini-Study metric was expressed in Box 3.2. With the simplifying convention

of normalised states, its square may be expressed as

$$ds^2 = \langle d\psi | d\psi \rangle - \langle d\psi | \psi \rangle \langle \psi | d\psi \rangle. \quad (3.53)$$

Invoking the time-dependent Schrödinger equation,

$$|d\psi\rangle = -iK |\psi\rangle dt, \quad (3.54)$$

this expression can be related to the driving Hamiltonian $K(t)$ in a general fashion by writing it as

$$ds^2 = [\langle \psi | K^2 | \psi \rangle - (\langle \psi | K | \psi \rangle)^2] dt^2 = (\Delta E)^2 dt^2 \quad (3.55)$$

where K and $|\psi\rangle$ are both time-dependent. A relationship to the generalised MT speed limit (Equation (3.10)) will be discussed just below. It already becomes apparent here. Consider parallel, global driving

$$K_{\mathcal{P}}^{(N)} := \sum_j K_j \bigotimes_{k \neq j} \mathbf{I}_k, \quad (3.56)$$

expressed in terms of local Hamiltonians K_j . Inserting this definition and the expression $|\psi_{\mathcal{P}}\rangle = \bigotimes_j |\psi_j\rangle$ into Equation (3.55), the desired result is obtained

$$\begin{aligned} ds_{\mathcal{P}}^2 &= \sum_j \langle \psi_j | K_j^2 | \psi_j \rangle + \sum_j (\langle \psi_j | K_j | \psi_j \rangle)^2 \\ &= \sum_j ds_j^2. \end{aligned} \quad (3.57)$$

Accordingly, the path length in the parallel case scales with $\sqrt{N}$. Relating this result back to the MT speed limit, it seems to explain part of the speedup: the minimum evolution time dictated by the speed limit scales linearly with the path length $\mathcal{L}$. Since

both the global and the single wit evolution follow geodesic trajectories (which is why Equation (3.52) holds) driving must satisfy the speed limit in both cases. Contrarily, in the parallel driving case the evolution does not follow a globally geodesic path but instead follows one which is $\sqrt{N}$ -times longer. We expect an increase in driving time with $\sqrt{N}$ as a consequence.

This still leaves the other factor of $\sqrt{N}$ unaccounted for if we want to explain the demonstrated speedup proportional to N . This second factor is explained by noting that the speed limits which bound the evolution with $K_{\mathcal{P}}$ and $K_{\mathcal{G}}$, respectively, in fact differ by a factor $\sqrt{N}$. The difference between the two cases lies in the respective integrands in Equation (3.11) which is effectively the square root of Equation (3.55) divided by dt^2 :

$$\Delta E := \sqrt{\langle \psi | K^2 | \psi \rangle - (\langle \psi | K | \psi \rangle)^2} \quad (3.58)$$

Separately expressing this relation for the entangling (Equation (3.35)) and parallel case (Equation (3.33) and Equation (3.56)) in terms of the single wit driving (i.e., $K = \frac{1}{2}E_{max}\sigma_x$ for $\phi_0 = 0$) the following relation is obtained:

$$\frac{1}{\Delta E^{\mathcal{P}}} = \sqrt{N} \frac{1}{\Delta E^{\mathcal{G}}}. \quad (3.59)$$

We consequently conclude that the speedup is reflected in equal parts by differences in the speed limits and the path length:

- 1) With the Bures angle $\mathcal{L}$ between input and output state fixed, the speed limit for parallel driving is $\sqrt{N}$ -times larger than that for the entangling evolution in the example.
- 2) In addition to the larger speed limit, the parallel evolution also takes a path which is $\sqrt{N}$ -times longer than the geodesic distance $\mathcal{L}$.

- 3) Taking these two points taken together, we observe a speedup proportional to N , the number of wits.

Before concluding, a few sentences are in order to comment on the relationship between the operations studied in this chapter and realistic implementations in the lab. This is discussed in the following section.

3.6.2 Implementability

The Hamiltonians $K_{\mathcal{G}}^{(N)}$ and $K_{\mathcal{T}}^{(N)}$ used in the above examples are highly non-local. In a realistic setting one might expect a Hamiltonian that consists of (local terms and) pairwise interactions alone, i.e.,

$$K_{pw} = \sum_{\langle m,n \rangle} K^{(m,n)} \quad (3.60)$$

where we have omitted an index to indicate N -dependence as well as identity operations on unaffected subsystems. For the case of qubits, $K^{(m,n)}$ would be expressed in terms of a symmetric basis of $SU(4)$, e.g. $K^{(m,n)} = \hat{\sigma}_x^{(m)} \otimes \hat{\sigma}_x^{(n)}$. As before, if the operator norm of $K^{(m,n)}$ is bounded by E_{max} the norm of K_{pw} should be bounded by NE_{max} to allow for a fair comparison. As a further simplification, the eigenvalues of the pairwise interaction terms $K^{(m,n)}$ may be assumed to be independent of N . For $N = 2$, $K_{\mathcal{G}}$ can be implemented by $K_{pw} = \hat{\sigma}_x^{\otimes 2} - \hat{\sigma}_y^{\otimes 2}$. For larger N , $K_{\mathcal{G}}$ cannot be expressed in the form of K_{pw} .

Nonetheless, prominent results exist which show that any given unitary operation on a system composed of qubits may be constructed from single-, and two-qubit gates [Nielsen et al., 2006]. It would be an interesting avenue for further research to start with these results and to relate them back to the minimum time necessary to accomplish a given unitary operation (composed of single- and two- qubit gates). In a second step, a relation to powerful evolution may be revealed. Moreover, one may

investigate interactions that are not only pairwise but more generally M -wise and ask how a quantum speedup scales with M .

A second limitation of the given analysis is that it was, for the largest part, restricted to wits and arrays of wits. The concept of quantum batteries, however, is more general and extends beyond such low-dimensional systems. The restriction to wits here was rather motivated by two considerations: (1) In quantum information theory it is usually presumed that larger systems can be understood sufficiently in terms of a collection of qubits (as pointed out in the previous paragraph). In how far this rationale extends from questions of computational complexity to questions of powerful evolution, however, remains unclear. (2) As we have seen in this chapter, under restriction to wits, an analytical understanding of the problem of powerful charging can be gained. A completely general solution was found for power-optimal single wit driving. In the case of arrays of wits we made additional assumptions in order to further simplify the problem. It is clear that when larger dimensions are to be taken into account for the study of powerful evolution, the limits of analytical results are quickly reached. Extending the intuition gained in the present studies to such a context will rather rely, for instance, on a variational approach. The problem can indeed, somewhat analogous to the quantum brachistochrone, be phrased in the language of variational optimisation. This question is currently being investigated [Binder et al., 2015b; Vinjanampathy et al., 2016].

3.7 Conclusion

The fact that limitations on the evolution speed of a system would be depend on the energy scales of the mechanism that causes the evolution seems intuitive. In quantum physics this dependence becomes explicit with the expression of quantum speed limits (Box 3.1) and the corresponding intuition carries over to the study of power. This

chapter was dedicated to the pursuit of optimising power, or more generally, the target function $\mathcal{F} = \frac{W}{T^\alpha}$, in unitary evolution. A phrasing of the analysis in the technology-inspired framework of battery charging aided the understanding that here not one but two, a priori independent, energy-scales are of relevance. The first one, the internal energy, is determined by the reference Hamiltonian H . The external energy scale, on the other hand, is reflected in the driving mechanism $K(t)$. While the latter equally acts on the system during the period of evolution (but not before or after), its magnitude is determined by constraints external to the system itself. It is these external energy bounds which limit the evolution speed and the maximal power.

The results of this chapter are two-fold. First, we developed an analytical solution which specifies an optimal driving protocol for the powerful charging of a single work bit. In a second step, we effectively turned the study of power into a question of optimal process duration by a priori fixing the initial and final energy. This simplification allowed us to study larger systems by examination of suitable examples. Hence we have shown that, when global charging of N wits is permitted, an advantage in power per wit proportional to N can be achieved compared to the local case. In these considerations, initial and final states of the evolution were required to be separable – an assumption justified by a usage scenario where batteries can be charged globally but are used (discharged) locally. Nonetheless, it would be an interesting extension of the present work to consider more general scenarios where, for instance, entangled output states are permitted. If a protocol of global charging and local usage is to be upheld in such scenarios one would observe *degrading* of the battery – that is, a loss of purity in each charge/discharge cycle. Furthermore, in order to allow for realistic noise and decoherence processes it will be important to generalise the approach presented here to open systems. This pursuit may be aided by the results of the

following chapter, where general (i.e., not necessarily unitary) quantum evolution is considered.

Energetics of general quantum processes

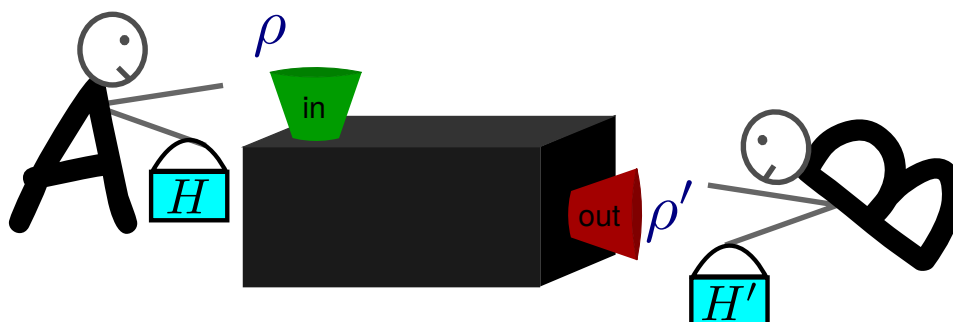


Figure 4.1: Cartoon representation of a completely-positive and trace-preserving (CPTP) process. A formal description of CPTP maps is given in Appendix B. For the present purposes, this cartoon representation captures the necessary details: Alice – equipped with a laboratory characterised by the reference Hamiltonian H – provides an input state ρ . The CPTP process outputs a state ρ' which is then at Bob’s disposal for work extraction in his laboratory characterised by the reference Hamiltonian H' . What are the energetics of this operation? How much work can Bob and Alice extract in their respective laboratories, and what part of the energy change should be considered heat?

This chapter establishes a first-law-like expression for the energetics of a CPTP process. In doing so, it establishes a distinction between equilibrium quantities, called *adiabatic work* and *operational heat*, and a genuinely out-of-equilibrium quantity based on the previously introduced concept of ergotropy. The meaning of the expression is obtained from an operational perspective by considering the work that could be extracted both from the input as well as the output state. Here, considering the energetics of a decoherence process helps to establish a context and understanding for operational heat. Subsequently, we demonstrate a relationship to an operational form of the second law and consider thermal and unital maps as specific examples in this context. This allows us to specify a criterion for positivity of the operational heat which employs the concept of majorisation introduced in Chapter 2.

The main results of this chapter were published in the article [Binder et al., 2015a]. The original contribution of these research findings is a thermodynamic characterisation of general quantum processes (i.e., CPTP processes). Importantly, by making an operational identification of the amount of work that may be extracted from input and output states, respectively, these results are applicable to processes governed by strong coupling.

The evolution of a closed quantum system is governed by the time-dependent Schrödinger equation. Given an input state ρ and a (generally time-dependent) Hamiltonian $K(t)$, the output state $\rho' := \rho(T)$ is unambiguous: it can be calculated with the help of the evolution operator defined by Equation (B.22). In this scenario, the energy difference $\Delta E = \text{tr}[\rho(T)K(T)] - \text{tr}[\rho K(0)]$ may safely be considered work as pointed out before. It is now a sensible question to ask

What are the energetics of a quantum process that is more general than unitary dynamics?

In order to address this question, we note that in quantum information theory a much more general quantum evolution than unitary processes is in fact commonplace: CPTP maps. Such maps describe any evolution that takes a state ρ to a state ρ' , subject to two physically (almost) minimal conditions:

- 1) **Complete positivity (CP):** It is impossible to end up with a state ρ' that has negative eigenvalues, even when system composition or the consideration of subsystems is taken into account.
- 2) **Trace preservation (TP):** For a normalised input state ($\text{tr}[\rho] = 1$), the trace of the output state ρ' also has to be exactly one.

Remembering that the eigenvalues of a quantum state (or more generally, the populations in any basis) can always be interpreted as the probabilities for the different measurement outcomes of some observable, both of these requirements appeal to intuition: (1) Negative probabilities are forbidden (for any conceivable measurement of the state or a subsystem); and (2) the probabilities must sum to one – i.e., we can be certain that some outcome will be measured. The results presented here rely on both of these conditions but are not contingent on a specific description of the maps (for instance, in terms of Kraus operators). CPTP maps may here in fact be thought of as an input-output formalism for quantum states as illustrated by the cartoon in Figure 4.1.

At this point is worth re-emphasising that quantum evolution – for instance, with a given CPTP map – does not by itself provide access to the energetics of the process. In addition, the specification of an energy landscape in the form of reference Hamiltonians at the time of the energy measurements is required. This is also captured by the cartoon representation above.

CPTP maps are ubiquitous in modern quantum physics and arguably the most generic, commonly employed description available for quantum processes. They may

be used to describe all processes which can be implemented by coupling the system to an initially uncorrelated ancilla, joint unitary evolution, and finally ‘tracing out’ over the ancilla (i.e., discarding it). In the context of this chapter, we will consequently refer to evolutions that are CPTP as ‘general quantum processes’.

Nonetheless, it should be noted at this point that even CPTP evolution is not the most general, conceivable evolution of a quantum system and the two restrictions – complete positivity and trace preservation – could be relaxed further. For instance, an experimenter could choose to *post-select* certain outcomes. Taking the example of a scattering experiment, a particle detector may in practice only cover a certain solid angle. Any particle that gets scattered outside of that solid angle will not be detected. Consequently, the probability of measuring it will be less than unity and trace-preservation would not be fulfilled in this example. Another generalisation would be to allow for processes which reflect initial correlations between the system described by ρ and some ancilla system, hence doing away with the requirement of complete positivity [Pechukas, 1994; Shaji and Sudarshan, 2005].

Were the CPTP restrictions to be relaxed along these lines, however, basic thought experiments like Maxwell’s demon or Landauer’s erasure could no further be resolved. Generalisations like the ones just outlined hence seem to be unlikely candidates for producing useful thermodynamics statements.

In analogy to the first law of thermodynamics we now discuss work done, extractable work, and heat for input-output processes described by CPTP maps. The concepts of ergotropy, *adiabatic work*, and *operational heat* – the latter two to be introduced in the following section – will allow us to state this chapter’s main result: an operational first law for general quantum processes. We subsequently link this result to known operational versions of the second law which apply in the same context.

Both the main result and its application to the operational version of the second law are supported by boxed examples. In this chapter, these examples in fact serve

a larger purpose than mere illustration. They are used to contextualise the more general results in particularly relevant limits, hence giving the main results their physical meaning.

4.1 Thermodynamics of input-output processes

In Chapter 1 we noted that the first law of thermodynamics, which establishes a distinction between work and heat, may be expressed in infinitesimal form by taking the differential of the internal energy $E = \text{tr}[\rho(t)K(t)]$, leading to the following expressions:

$$\delta W = \text{tr}[\rho(t)\dot{K}(t)]dt \quad (1.14')$$

$$\delta Q = \text{tr}[K(t)\dot{\rho}(t)]dt, \quad (1.15')$$

where we have now explicitly expressed time-dependence and indicated derivatives with respect to time by a dot. We point out again that unitarity is not assumed here and that $\rho(t)$ is generally not determined by the Liouville-von Neumann equation in terms of $K(t)$. If the evolution of $\rho(t)$ were unitary and due to $K(t)$ we would have $\delta Q = 0$.

Integrating Equations (1.14) and (1.15) over a specific evolution (average) expressions for work and heat may be obtained:

$$\begin{aligned} \Delta E &= \int_0^T \delta W + \int_0^T \delta Q = W + Q \\ &= \text{tr}[\rho(T)K(T)] - \text{tr}[\rho(0)K(0)]. \end{aligned} \quad (4.1)$$

Here, as pointed out before, the energy difference ΔE depends only on the endpoints of the process at times $t = 0$ and $t = T$. Heat and work, on the other hand, are path-dependent.

For CPTP processes, a prescription of what is work and what is heat along these same lines is in general not possible. This is because the integrands in Equation 4.1 are often neither well-defined nor easy to measure. Only for systems with well-defined descriptors of $\rho(t)$ and $\dot{\rho}(t)$ do we have a closed form for work and heat. For instance, Markov systems may be described in a time local form $\dot{\rho}(t) = \mathcal{L}[\rho(t)]$ in terms of a Liouvillian super-operator $\mathcal{L}$, leading to the well-known results by Alicki [1979]. More generally, such explicit time-dependence relies on (closely related) assumptions about weak coupling, semigroup properties of the quantum channel, or its infinitesimal divisibility. Here, we are specifically interested in the regime where such assumptions do not hold. In this sense our approach shares similar obstacles with the popular description of thermal operations (cf. Box 2.5). What is different in the present scenario is that we do not impose strict energy-conservation (for instance, in order to derive a second law) but rather ask:

Can we meaningfully characterise the energy exchange in a quantum process for which dynamic resolution is not available?

It is clear that trying to recover path-dependent quantities like Equations (1.14) and (1.15) would be futile from the outset since the ‘path’ (that is, the precise system dynamics) is either unknown or not well defined.

The minimal requirements for the present approach are the existence of meaningful marginals of the system state and Hamiltonian at both the beginning and the end of the process (Restrictively, one could ask for the system-ancilla state to be separable initially and for the total reference Hamiltonian to be a sum of two local Hamiltonians). However, neither the (marginal) system state nor a system Hamiltonian need to be available and moreover thermodynamically meaningful *during* the time-resolved evolution. Far from being an academic issue, this is a very realistic and practical problem. For instance, in a chemical process the Hamiltonian dynamics as well as the reduced state at all times are generally not known. Such stochastic processes can be

described by a CPTP map, which, as suggested above, may be thought of as a black box relating an input to an output state.

In this context, work and heat obtain their meaning in an operational sense:

Given a general map $M(\rho)$, how much work can be extracted from the output state $\rho' := M(\rho)$ assuming a fully controllable quantum operation?
How much energy is wasted (or gained) in the process?

The resource-theoretically-minded reader may think of the initial state and the map M as being ‘free’ in this scenario.

In the following section we proceed by first briefly revisiting the concept of ergotropy before introducing an operational quantity called *adiabatic work* which will then allow us to state the main result.

4.2 Energetics of open quantum evolution

In this section the chapter’s main result is presented after first briefly revisiting the concept of ergotropy extraction, followed by the introduction of a quantity called *adiabatic work*.

4.2.1 Ergotropy revisited

In order to derive a general expression for the energy change of a quantum process we start with the simplest scenario: cyclic, unitary work extraction as presented in Section 2.2. The maximum work that can be extracted from an active state ρ with respect to a Hamiltonian H via a cyclic unitary process ($\rho \rightarrow \pi$) is given by the ergotropy

$$\begin{aligned} \mathcal{W}(\rho, H) &:= \text{tr}[(\rho - \pi)H] \\ &= \sum_{m,n} r_m \epsilon_n \left[|\langle \epsilon_n | r_m \rangle|^2 - \delta_{mn} \right], \end{aligned} \tag{2.14}$$

where we have retained the same notation as before, to wit:

$$H := \sum \epsilon_n |\epsilon_n\rangle\langle\epsilon_n|, \text{ with } \epsilon_{n+1} \geq \epsilon_n \forall n, \quad (2.5)$$

$$\rho := \sum r_n |r_n\rangle\langle r_n|, \text{ with } r_{n+1} \leq r_n \forall n. \quad (2.6)$$

4.2.2 Adiabatic work

In a different scenario, let us also consider a non-cyclic, unitary process with different initial and final Hamiltonian – H and

$$H' := \sum \epsilon'_n |\epsilon'_n\rangle\langle\epsilon'_n|, \text{ with } \epsilon'_{n+1} \geq \epsilon'_n \forall n. \quad (4.2)$$

If we restrict the change in the Hamiltonian from H to H' (suitably parametrised) to be adiabatic in the quantum sense, i.e., the eigenstates of the Hamiltonian remain eigenstates at each instant in time, the final state π' will be a passive state with respect to H' if the initial state π_m was passive with respect to H . Since this transformation is unitary there is no heat and we call the energy change *adiabatic work*¹:

$$W_{ad} = \text{tr}[\pi' H'] - \text{tr}[\pi_m H]. \quad (4.3)$$

In the following we will associate this definition with any process, adiabatic or not, that starts with a passive state and preserves the state's spectrum as well as keeping it diagonal in the basis of the reference Hamiltonian.

In the case of a general unitary process $(\rho, H) \rightarrow (\rho', H')$ we can combine the ideas of ergotropy and adiabatic work. Since all energy change is work in this scenario (due to unitarity) it can be extracted reversibly from the final state if full quantum control

¹Allahverdyan and Nieuwenhuizen [2005] used the same term in a similar context but specifically for quantum-adiabatic processes. The present definition differs in that it will also be used in the context of non-adiabatic processes.

is available. Here, the extraction process ends with the initial Hamiltonian H . The extractable work in ρ' is thus given by

$$W = W_{ad} + \mathcal{W}(\rho', H') - \mathcal{W}(\rho, H). \quad (4.4)$$

If the initial state is passive in such a process one may think of the ergotropy as *deposited work*, or *inner friction* like Plastina et al. [2014], who considered initial Gibbs states.

4.2.3 General energetics

We are now ready to consider the internal energy change ΔE due to general quantum evolution with some CPTP map M , i.e., $\rho \rightarrow \rho' := M(\rho)$:

$$\Delta E = \text{tr}[\rho' H'] - \text{tr}[\rho H], \quad (4.5)$$

where we have again labelled the initial and final system Hamiltonian H and H' , respectively. We may now use the notions of ergotropy and adiabatic work – as introduced in the previous section – in order to arrive at an operationally meaningful first law of thermodynamics. Defining the intermediate passive state

$$\pi_m := \sum_n r'_n |\epsilon_n\rangle \langle \epsilon_n|, \quad (4.6)$$

we add and subtract $\text{tr}[\pi' H']$, $\text{tr}[\pi_m H']$, and $\text{tr}[\pi H]$ to Equation (4.5) to obtain

$$\begin{aligned} \Delta E = & \text{tr}[\pi H] - \text{tr}[\rho H] + \text{tr}[\rho' H'] - \text{tr}[\pi' H'] \\ & + \text{tr}[\pi' H'] - \text{tr}[\pi_m H'] + \text{tr}[\pi_m H] - \text{tr}[\pi H]. \end{aligned} \quad (4.7)$$

In this equation, the first two pairs of terms are simply the ergotropies

$$-\mathcal{W}(\rho, H) + \mathcal{W}(\rho', H') =: \Delta\mathcal{W}, \quad (4.8)$$

while the next pair is adiabatic work. Defining *operational heat*

$$Q_{op} := \text{tr}[\pi_m H] - \text{tr}[\pi H], \quad (4.9)$$

we state this chapter's main result:

$$\Delta E = \Delta\mathcal{W} + W_{ad} + Q_{op}. \quad (4.10)$$

This equation tells us that the internal energy change in a general quantum process can be split up into a work-like, a heat-like and a third, genuinely out-of-equilibrium contribution which equals the difference in ergotropy between initial and final state. In this sense it may be understood as an operational first law of quantum thermodynamics. The definition of heat satisfies intuition as the eigenvalues of the equilibrium state π_m are changed to attain another equilibrium state π , in analogy to Equation (1.15).

The derivation of Equation (4.10) has been of an arithmetic nature, somewhat removed from physical intuition. The rest of this chapter is devoted to scrutiny of the equation's physical meaning, aligning it with an operational perspective, and analysing relevant limiting cases in boxed examples.

Firstly, we note that Equation (4.10) becomes particularly meaningful for processes where the internal energy remains constant but the ergotropy of the state changes. A conventional description of the first law is inadequate for recognising this change. Such a scenario is illustrated in Example 4.1.

Example 4.1: Operational heat and decoherence

We consider a system-ancilla composition which is originally in a product state $\rho \otimes |\phi\rangle\langle\phi|$. We return to equation Equation (2.37) and write the full Hamiltonian as

$$H_{SA} = H_S \otimes \mathbf{I}_A + \mathbf{I}_S \otimes H_A + H_I. \quad (2.37')$$

Thus, the Hamiltonian is again split into three separate parts for system, ancilla, and the interaction between the two, respectively. While we assume H_S to be time-independent, H_I may generally depend on time. The induced dynamics may, as per usual, be expressed by an evolution operator $U(t)$ acting on the composite system, yielding the local system state

$$\rho(t) = \text{tr}_A[U(t)\rho \otimes |\phi\rangle\langle\phi| U^\dagger(t)], \quad (4.11)$$

where $\rho := \rho(0)$. We now assume that the system Hamiltonian commutes with the interaction Hamiltonian, $[H_S, H_I] = 0$ at all times. Consequently, the energy of the system with respect to H_S remains constant during the evolution (i.e., for H_I vanishing at the end of the process).

Moreover, work and heat also vanish. This is seen by recognising that the populations in the local state $\rho(t)$ in Equation (4.11) remain constant throughout the evolution: in the energy eigenbasis, $U(t)$ only introduces a phase on each eigenstate of H_S which squares to unity for the diagonal elements of $\rho(t)$. Consequently, work not only vanishes according to the simple prescription $\dot{W} = \text{tr}[\dot{H}_S \rho]$ but also according to the more sophisticated treatment in Box 2.6 (i.e., Equations (2.42) and (2.45)).

Crucially, however – and in spite of vanishing work and heat according to the conventional prescription, the ergotropy of the state generally changes during decoherence processes of the type just described.

For the sake of a more specific illustration, we may consider an example where system and ancilla are both given by a qubit and the evolution happens according to an interaction Hamiltonian $H_I = \sigma_z \otimes \sigma_z$ for $0 \leq t \leq \tau$. Starting with a generic state

$$\rho = \begin{pmatrix} p & c \\ c^* & 1-p \end{pmatrix} \quad (4.12)$$

and an ancilla state

$$\sigma = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix}, \quad (4.13)$$

the dynamics can be solved exactly:

$$\rho(t) = \begin{pmatrix} p & c \cos 2t \\ c^* \cos 2t & 1-p \end{pmatrix}. \quad (4.14)$$

It is apparent that while the state's internal energy does not change (for a local Hamiltonian in σ_z -eigenbasis) the ergotropy in fact decreases due to a loss of coherence (Periodic revival occurs at times $t = \frac{n}{2}\pi$ with $n \in \mathbb{N}$). According to the main result of this chapter, the negative change in ergotropy is compensated by an operational heat flow into the system, i.e., $\Delta\mathcal{W} = -Q_{op}$.

This result holds true in general, i.e., for systems of arbitrary dimension and all interaction Hamiltonians – time independent or not – which commute with the system Hamiltonian, $[H_I, H_S \otimes \mathbf{I}_A] = 0$. As noted above, the populations of the state remain constant in such decoherence processes while the coher-

ences change over time due the open systems dynamics, leading to a change in ergotropy. This ergotropy change is compensated by operational heat.

The operational view taken here is hence illuminating for the thermodynamics of decoherence processes in general. It is relevant, for instance, in decoherence scenarios such as the ones which may be described in terms of a master equation [Breuer and Petruccione, 2002; Schlosshauer, 2007].

Turning the attention back to Equation (4.10), we may now interpret the CPTP map as a sequence of fictitious thermodynamic processes as illustrated in Figure 4.2. In particular, we consider work extraction from the analogue of Bob's perspective in Figure 4.1 and ask

How much work may be extracted from ρ' and how much heat has to be invested in order to return to the initial state ρ ?

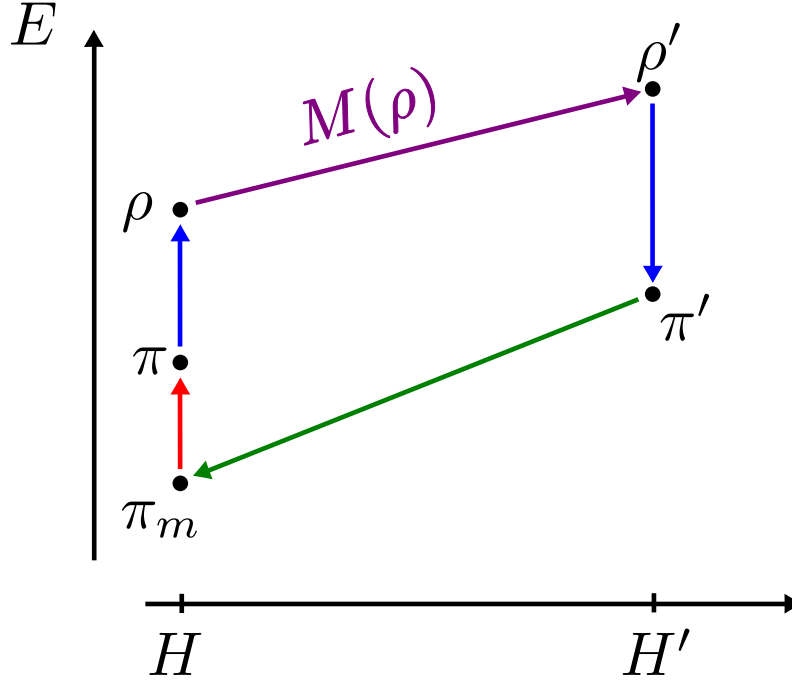


Figure 4.2: The process starts with a non-passive state ρ and ends up in state $\rho' := M(\rho)$. We express this out-of-equilibrium change in internal energy between ρ and ρ' (purple) using the plausible, but not necessarily implemented, reverse process of first extracting ergotropy $\rho' \rightarrow \pi'$ (blue), followed by equilibrium extraction of adiabatic work $\pi' \rightarrow \pi_m$ (green), equilibrium heating $\pi_m \rightarrow \pi$ (red), and finally re-depositing of ergotropy $\pi \rightarrow \rho$ (blue), to close the loop. The relationship between the corresponding energy changes is given by Equation 4.10. The horizontal axis represents the reference Hamiltonian's parameter space and the vertical axis the internal energy.

Importantly, the processes represented by the arrows do not follow the corresponding paths in the depicted space and the arrows are merely meant to indicate the connections and energy differences of the corresponding processes.

The energy changes $\mathcal{W}(\rho, H)$ and $\mathcal{W}(\rho', H')$ corresponding to the blue arrows are always non-negative. Conversely, W_{ad} and Q_{op} , corresponding to the green and red arrow, respectively, may have either sign. While the depicted processes need not be implemented in practice, they are operationally meaningful as illustrated below.

Considering the reverse process, the state ρ' is at disposal for work extraction. In this scenario, maximal cyclic work extraction simply yields $\mathcal{W}(\rho', H')$ as previously described in Chapter 2.

If, more generally, a non-cyclic process is considered, an amount of work equal to $\mathcal{W}(\rho', H') + W_{ad}$ may be extracted. This amount is indeed maximal for a unit-

ary protocol starting with ρ' if the process is required to end up with the reference Hamiltonian H . After work extraction the system ends up in state π_m .

Next, in order to complete the cycle by also resetting the state, a heat step is necessary to return to the original spectrum of ρ . The heat in this process, going from π_m to π , is given by $-Q_{op}$.

Finally, coherences and excitations which might have been present in ρ are restored by re-depositing $\mathcal{W}(\rho, H)$ into the system. This last step is of course only necessary if the initial state was active. For illustration we now provide a physically relevant example where this is not the case (Example 4.2).

Example 4.2: Initial thermal state

In a particularly relevant setting we may assume the principal process of Figure 4.2 to start in a thermal state $\tau_\beta = \rho = \pi$. This is indeed a natural limiting case to consider if, similar to thermal operations, a heat bath at inverse temperature β is available as a free resource. The setting is the same as in Figure 4.2 with $\pi = \rho$. Consequently, no additional deposition of ergotropy is possible at the end of the reverse work extraction. As before, the ergotropy gained in going from ρ' to π' is the maximum work that can be extracted in a cyclic process with initial state ρ' and reference Hamiltonian H' .

The maximum work that can unitarily be extracted in a non-cyclic process with final Hamiltonian H , on the other hand, is given by $W_{max} := \mathcal{W}' + W_{ad}$. While $\mathcal{W}'$, being a genuinely out-of-equilibrium quantity, is always positive, W_{ad} could also be negative. Requiring the process to finish with H (rather than H') could thus in fact be disadvantageous for work extraction since, depending on H , $W_{max} < \mathcal{W}'$ is possible.

In the last step (the red arrow in Figure 4.2), the transfer of operational heat when going from π_m to $\pi(= \tau_\beta)$ corresponds to the very practical scenario of

thermalisation at the initial temperature β and Hamiltonian H after maximal work extraction.

In summary we note that it has long been convenient to express the properties of out-of-equilibrium systems by using quantities which relate to equilibrium states and hence can be computed in a straight-forward fashion. Furthermore, the equilibrium quantities relate to measurements that can predict the non-equilibrium properties of systems of interest. Similar to other works in statistical mechanics [Esposito et al., 2009; Campisi et al., 2011] we have broken up the out-of-equilibrium energy change into equilibrium quantities adiabatic work and operational heat, and the operational quantity ergotropy.

With the intuition for the operational heat, gained in Examples 4.1 and 4.2, in mind we now relate the operational first law, expressed by Equation (4.10), to an operational second law of thermodynamics.

4.3 Connecting first and second laws

In Chapter 1, we used the relative entropy between a state ρ and a thermal state τ_β in order to demonstrate a quantum version of the Clausius inequality. For systems in equilibrium, owing to the notions of temperature β , thermodynamic entropy ΔS , and heat Q being well defined, we may state the second law as

$$\Delta S \geq \beta Q \tag{1.23}$$

Focussing again on more general quantum processes, we first note that a statement of the second law which is relevant to CPTP maps is in fact also well known [Spohn, 1978; Hatano and Sasa, 2001; Sagawa, 2012]. We may, in a similar spirit to before, invoke the relative entropy to derive it. In particular, we note that relative entropy,

defined as

$$R(\rho\|\sigma) := \text{tr}[\rho \log \rho] - \text{tr}[\rho \log \sigma], \quad (1.6)$$

obeys contractivity under application of a CPTP map M [Lindblad, 1975]:

$$R(\rho\|\sigma) \geq R(M(\rho)\|M(\sigma)). \quad (4.15)$$

Since we are interested in the entropy change $\Delta S := S(M(\rho)) - S(\rho)$, we have the choice of a reference state σ . A natural choice of σ is a fixed point ϕ of the map M , i.e., $M(\phi) = \phi$. Rearranging the contractivity inequality, we thus arrive at the quantum version of the Hatano-Sasa inequality [Spohn, 1978; Hatano and Sasa, 2001; Sagawa, 2012; Vinjanampathy and Modi, 2015]:

$$\Delta S \geq -\text{tr}[(M(\rho) - \rho) \log(\phi)]. \quad (4.16)$$

While the first law relates to the partitioning of energy into heat and work, the (Clausius form of the) second law relates only to the increase in entropy. Specifically, the quantum Hatano-Sasa inequality is valid for CPTP evolution where neither heat nor temperature are well defined quantities. Hence, in general it is difficult to verify the internal consistency between a quantum generalization of the first law and a similar generalization of the second law that is applicable to arbitrary CPTP dynamics. Nonetheless, we are able to draw a relation between the two laws by considering thermal maps in Example 4.3.

Example 4.3: Thermal maps

Thermal maps were defined by Equation (2.36) as those CPTP maps which have a specific thermal state $\tau_\beta = \exp[-\beta(H - F)]$ as a fixed point, i.e., $M_\beta(\tau_\beta) = \tau_\beta$. Due to these maps (also called *Gibbs-preserving* maps) being a superset of

thermal operations^a, all results related to thermal maps presented here equally apply to the popular set of thermal operations.

In order to make the connection to the second law, a cyclic process is considered, i.e., $H = H'$. The input and output states ρ and ρ' are not restricted and may both be out-of-equilibrium. The quantum Hatano-Sasa inequality now reduces to the familiar version of the second law:

$$\begin{aligned}\Delta S = S(\rho') - S(\rho) &\geq -\text{tr}[(\rho' - \rho) \log(\phi)] \\ &= \beta \text{tr}[(\rho' - \rho)(H - F)] \\ &= \beta (\Delta \mathcal{W} + Q_{op}),\end{aligned}\tag{4.17}$$

with the change in ergotropy $\Delta \mathcal{W}$ playing the role of heat along with Q_{op} . This restatement of the quantum Hatano-Sasa inequality is interesting in that it lower-bounds the entropic change by the sum of two terms, the change in ergotropy and the operational heat, which are both measurable and operationally well defined. It is worth noting that both of these quantities may in fact be negative.

^aThat is, any thermal operation constitutes a thermal map. The inverse, however, is not true: there are thermal maps which may not be implemented by a thermal operation. This was further elaborated by Faist et al. [2015].

4.4 Majorisation, entropy, and operational heat

In order to give a condition for when operational heat Q_{op} is positive (negative), we return to the concept of majorisation which was introduced in Box 2.3. A state ρ is said to majorise ρ' (written $\rho \succ \rho'$) if the eigenvalues of the two states satisfy

$$\sum_{m=1}^n r_m \geq \sum_{m=1}^n r'_m \quad \forall n,\tag{2.16'}$$

where ρ is defined by Equation (2.6) and, analogously,

$$\rho' := \sum_m r'_m |r'_m\rangle \langle r'_m|, \text{ with } r'_{m+1} \geq r'_m. \quad (4.18)$$

Note that, due to the fact that some states are incomparable (i.e., they do not obey a majorisation relation), we cannot make a statement about operational heat based on the states alone in such cases: it will also depend on the energy eigenvalues.

Majorisation now in fact provides a sufficient criterion for operational heat to be positive (negative):

$$\rho \succ \rho' \Rightarrow Q_{op} \geq 0, \text{ and} \quad (4.19)$$

$$\rho \prec \rho' \Rightarrow Q_{op} \leq 0. \quad (4.20)$$

The proof of Equation (4.19) is straightforward (and the proof of Equation (4.20) is exactly analogous):

Since the eigenvalues of the states do not change during ergotropy extraction $\rho \succ \rho'$ implies $\pi \succ \pi'$ (and vice versa). Examining the expression for Q_{op} we have:

$$\begin{aligned} Q_{op} &= \text{tr}[\pi' H] - \text{tr}[\pi H] = \sum (r'_n - r_n) \epsilon_n \\ &= \sum_n (\epsilon_{n+1} - \epsilon_n) \sum_{m=1}^n (r_m - r'_m), \end{aligned} \quad (4.21)$$

where each term in the last line is non-negative (due to Equation (2.16)).

In the same way, adiabatic work is non-negative if $H' \succ H$. Unlike for operational heat, there is, however, no connection between the majorisation relations for H and H' and the type of map that governs the process (cf. Example 4.4).

Moreover, if $\pi \succ \pi'$ then $f(\pi') \geq f(\pi)$ for any Schur-concave function f [Puchała et al., 2013]. In the present context, this means that $\rho \succ \rho'$ implies $S(\rho') \geq S(\rho)$ and therefore a non-negative entropy change $\Delta S \geq 0$. This implication is rather

profound: majorisation guarantees that both the entropy change and operational heat are positive simultaneously. We interpret this as a specific out-of-equilibrium analogue of the Clausius inequality, applicable to pairs of states (connected by a CPTP map) which obey a majorisation relation. In order to obtain an analogous statement for processes rather than pairs of states we consider the case of *unital* and *anti-unital* maps in Example 4.4.

Example 4.4: Unital maps

Unital maps M_u take the maximally mixed state onto itself:

$$M_u \left(\frac{\mathbf{I}}{d} \right) = \frac{\mathbf{I}}{d}. \quad (4.22)$$

This simple condition has strong consequences: according to the quantum Hardy-Littlewood-Polya theorem [Bengtsson and Życzkowski, 2006] the input state majorises the output state, $\rho \succ M_u(\rho)$, for any ρ if M_u is unital.

As a consequence of the majorisation arguments above, Q_{op} is thus non-negative for *any* input state ρ and *any* unital map M_u : for $\rho' = M_u(\rho)$, with M_u unital, the condition on the left of Equation (4.19) is always fulfilled. Moreover, the entropy change ΔS is also never negative for unital maps.

Conversely, for all non-unital maps, such as the thermal ones described in Example 4.3, there exists at least one state ρ (the maximally mixed one being a trivial example) that is majorised by the output state ρ' . In these cases, the amount of accessible work increases, i.e., the last term in Equation (4.21) is non-positive and therefore operational heat is less than or equal to zero. The change in entropy for such a process will also be non-positive. The directionality that comes with the second law of thermodynamics is here reflected in the asymmetry between unital and non-unital maps: a heat-like increase of a state's energy (and entropy) only requires a unital map, while extraction –

corresponding to a negative heat-like contribution – necessitates a non-unital channel. The representation of such a channel in terms of an ancilla makes clear that the second law is not ‘violated’ here.

In addition to unital maps we may formally define *anti-unital* maps as those maps for which any output state majorises the corresponding input state. In such a process the operational heat is never positive (i.e., the condition on the left of Equation (4.20) is always fulfilled), nor is the entropy change.

In the context of equilibrium thermodynamics, the second law guarantees that $Q \geq 0$, $\Delta S \geq 0$ and that the latter is at least as big as β times the former. But in the context of quantum thermodynamics, no such guarantee exists in general. Consequently, one can have cooling transformations that reduce the entropy of the states [Vinjanampathy and Modi, 2015]. Majorisation – for instance, as a consequence of unitality – strongly restricts the set of allowed transformations to those with positive operational heat and increasing entropy.

4.5 Conclusion

In summary, this chapter’s main result is the establishment of a relation that gives an explicit energy balance for all quantum processes that are completely-positive and trace-preserving (Equation (4.10)). Here, complete-positivity and trace-preservation guarantee that output states are in fact ‘physical’. For such processes we have operationally defined heat. Crucially, we have made use of the main result in formulating an operational framework for the thermodynamics of open quantum systems. The important feature of this framework is that it relies only on general quantum processes which connect input and output states. It provides an interpretation of operational heat and adiabatic work in terms of (fictitious) work extraction processes. For the case

of thermal maps, Example 4.3 draws a relation to thermodynamic out-of-equilibrium processes which rely on a free, single-temperature heat bath.

We have connected the operational first law to an existing version of the second law which is applicable to the same processes. In this context, both operational heat and entropy change were shown to be positive when the input majorises the output state (for instance, as a consequence of unitality), making an unambiguous connection between the two operational laws.

Furthermore, we have pointed out that the conventional thermodynamic description of quantum processes in terms of projective energy measurements alone does not suffice to capture the change in work value when coherences and excitations of the state are possible. This was illustrated by Example 4.1. For the decoherence scenarios described there, a change in extractable work (ergotropy) is compensated by an (operational) heat flow into the system, thus giving a concrete meaning to operational heat.

Conclusions and outlook

“[...] science, in the very act of solving problems, creates more of them.”¹

Abraham Flexner

“The important thing is not to stop questioning.”²

Albert Einstein

In the preceding chapters we set out to understand and optimise quantum operations from a thermodynamic perspective – that is, taking the tools of quantum information theory, such as CPTP maps, we pursued a prescription of thermodynamic meaning to the corresponding processes.

To this aim, Chapter 1 introduced the framework of thermodynamics and its laws. The laws were subsequently motivated from a statistical mechanics point of view, adopting language and formalism of quantum information theory. The chapter

¹[Flexner, 1930]

²Quoted by Miller [1955]

concluded with a consideration of the boundaries of conventional, equilibrium thermodynamics and a perspective on the role of quantum phenomena in going beyond these boundaries.

Building on the basic concepts from Chapter 1, we introduced the notion of passivity as a more general form of thermodynamic equilibrium (compared to Boltzmann-Gibbs-thermality) when considering finite-size systems in Chapter 2. Passivity gained its meaning from the analysis of unitary, cyclic work extraction. The final part of the chapter was devoted to providing a wider context of thermodynamic work extraction from quantum systems, comparing classical and quantum approaches.

Having laid the groundwork in the first two chapters, we addressed the question of optimising unitary quantum processes for power in Chapter 3. For the exemplary case of qubit driving, we derived the chapter’s first main result: a power-optimal driving protocol (prescribed by Equation (3.25)), applicable to any given initial state. The study of power in this chapter was crucially motivated by the existence of quantum speed limits: if it was not for the speed limits no physical restriction to power would exist since any process could happen instantaneously. Terming the tuple of qubit and its thermodynamic reference Hamiltonian H a wit (short for ‘work bit’), we analysed the power required for unitary driving of an array of N wits. Further investigating the connection between driving speed and power, the chapter’s second main result demonstrated that when driving an array composed of N wits the time required for a full charge may be decreased by a factor of $1/N$ as compared to the single wit case (given the same operator norm constraint on the driving Hamiltonian). Thus, the power per wit may be N -fold increased by driving globally rather than locally. Even though this result holds for states which are separable at the beginning and at the end of the protocol, we demonstrated that the power enhancement relies on the possibility of entangling the array state during the driving. This established a strong

link between a genuinely quantum property (entanglement) and a thermodynamic advantage (enhancement of the maximal charging power).

The thermodynamic analysis of CPTP processes resulted in Chapter 4’s main result which is represented by Equation (4.10). It states that the energy exchange during a general quantum operation which starts in an arbitrary state ρ may be split into three parts: two equilibrium terms – adiabatic work W_{ad} and operational heat Q_{op} , and a third, non-equilibrium contribution $\Delta\mathcal{W}$ which corresponds to the change in ergotropy, i.e., the difference in work which may be extracted from the initial and final state, respectively, in a unitary cycle. We were able to give operational meaning to the chapter’s main result by considering work extraction from the output state ρ' with the operational requirement to end up back in the initial setting. All three of the contributions to the energy change – W_{ad} , Q_{op} , and $\Delta\mathcal{W}$ – may be either positive or negative and they accordingly correspond to work/heat which may either be extracted or has to be invested when reconstructing the initial state. Furthering the analysis, we showed that the operational view which led to the chapter’s main result has a straightforward meaning for specific, more constrained scenarios like decoherence (cf. Example 4.1). Finally, consideration of thermal and unital maps in the last part of the chapter (cf. Examples 4.3 and 4.4) allowed us to establish a connection to a recent formulation of the second law, applicable to the same class of processes.

Outlook

In the spirit of solving and creating more problems simultaneously – as epitomised by this chapter’s opening questions, it is important to corroborate the results in this thesis with a broader perspective on open questions, potential generalisations, and further avenues of research emanating from them.

On the topic of work extraction presented in Chapter 2, it is apparent that there remains more research to be done before a coherent picture and a full consensus will

emerge: so far the notions of work extraction from quantum systems apply to a range of different scenarios as outlined in Chapter 2. In particular, it will be interesting to understand the role of coherences in work extraction. Some progress in this direction has already been made by relating results to the framework of thermal operations, on one hand, and assessing the catalytic potential of quantum coherence, on the other.

Moreover, while experimental verification of some work-extraction results has already taken place, direct experimental applications, in particular for finite-size quantum systems, are still often missing and call for further investigation.

In Chapter 3, when considering work deposition (i.e., battery charging), the demonstrated speedup was explained with the appearance of quantum correlations during the charging process. This begs the question if a more general relationship can be established – perhaps an upper bound – for the relationship between charging speed (or, more generally: power) and the amount of entanglement permitted during the process. This question is in itself intricate since no unique notion of entanglement exists for entanglement between more than two subsystems. Alternatively, it would be interesting to investigate the possibility of bounding the speedup of the charging process in terms of some characteristic quantity related to the permitted interaction Hamiltonians. The interaction in the example, of the form $|0\rangle^{\otimes N}\langle 1|^{\otimes N} + |0\rangle^{\otimes N}\langle 1|^{\otimes N}$, is highly non-local. One might instead consider an interaction which only acts on K rather than all N subsystems. Lastly, the examples studied here were restricted to be locally two-dimensional (i.e., qubits) and an extension to higher dimensions may lead to further insights.

An interesting study that may follow from Chapter 4 is the further consideration of Example 4.1 and to study more generally the thermodynamics of decoherence, for instance as described by a corresponding master equation of the Born-Markov type. In addition, it is reasonable to wonder if the results may not be used to describe heat engines whose strokes are composed by CPTP maps. For instance, one could imagine

a scenario where an experimenter has a ‘free’ quantum channel at her disposal and one could then ask for a cyclic engine design which optimises some thermodynamic figure of merit like efficiency (carefully defined), or power.

The author plans to continue the research on these open questions and welcomes feedback and suggestions.

Proof of equivalence between complete passivity and thermality

In this appendix we proof that any completely passive state must be thermal and that, inversely, any thermal state is completely passive.

In other words: the set of completely passive states is identical to that of thermal states.

This proof follows the same logic as the one provided by Skrzypczyk et al. [2015].

We proceed as follows:

- 1) We re-formulate Equation (2.13) for three energy levels¹.

¹Remember that all passive qubit states are thermal. Passive but non-thermal states can consequently only exist in systems of at least three dimensions.

- 2) We introduce *virtual temperatures* and show that they are the same for each transition if and only if the state has Gibbs form².
- 3) For a passive (but not thermal) state π , we choose two transitions with different virtual temperatures in order to show in general how any such state may be activated by system composition – i.e., $\pi^{\otimes N}$. This is done by explicit construction of two N -partite levels with population inversion.

This completes the first part of the proof:

Any passive, non-Gibbs state may be activated.

- 4) In the last step we show the inverse – i.e.,

all Gibbs states τ_β remain thermal (and consequently, passive) under system composition – $\tau_\beta^{\otimes N}$,

hence completing the proof.

(1) We consider two energy levels of an N -partite system. The first one, $E_a = a\epsilon_0 + (N - a)\epsilon_l$, consists of the single system levels ϵ_0 and ϵ_l . The second one is simply given by $E_b = N\epsilon_m$. We further assume that $0 \leq \epsilon_0 < \epsilon_l < \epsilon_m$, and consequently, due to passivity, $\log r_0 \geq \log r_l \geq \log r_m$. Equation (2.13) may then be rewritten as

$$a\epsilon_m + (N - a)\epsilon_0 < N\epsilon_l \Rightarrow a \log r_m + (N - a) \log r_0 \geq N \log r_l, \quad (\text{A.1})$$

or, equivalently³,

$$\frac{a}{N} \frac{\epsilon_m - \epsilon_0}{\epsilon_l - \epsilon_0} < 1 \Rightarrow \frac{a}{N} \frac{\log r_0 - \log r_m}{\log r_0 - \log r_l} \leq 1. \quad (\text{A.2})$$

² For the sake of simplicity, ground states are here also referred to as Gibbs states (or, synonymously, thermal states), i.e., in the limit $\beta \rightarrow \infty$. They are not considered separately in this proof but it is straightforward to see that (1) ground states are passive; (2) the combination of ground states again yields a ground state; (3) all other passive states have at least two populated levels.

³We may here exclude cases where any of the populations are zero. The only such scenario relevant for this proof occurs for $r_m = 0$ and is treated separately below.

This relationship, being a subset of the conditions implied by Equation (2.13), has to be fulfilled by any three levels which fulfil the condition on its left-hand side. The same holds for the inverse relationship (i.e., with inequality signs turned around).

(2) We introduce the concept of a virtual temperature β_{kl} for any passive state π and any transition between levels ϵ_k and ϵ_l of the corresponding single-system reference Hamiltonian⁴:

$$\beta_{kl} := \frac{\log r_k - \log r_l}{\epsilon_l - \epsilon_k}. \quad (\text{A.3})$$

It is easily seen that for a thermal state τ_β , $\beta_{k,l} = \beta \ \forall \ k, l$. Conversely, for any passive, non-thermal state there are at least two transitions which do not share the same virtual temperature. This follows from the fact that for a passive state the relationship

$$\frac{r_n}{r_m} = \exp[-\beta(\epsilon_n - \epsilon_m)], \quad (\text{A.4})$$

in addition to requiring the state to be normalised, in fact fully defines a thermal state (given β and reference Hamiltonian H).

Concretely, we may first choose the transition between the ground level ϵ_0 and any higher energy level and then look for a second transition with the ground state that has a different virtual temperature. For the two non-ground levels we may always choose the labels l and m such that the above condition $\epsilon_0 < \epsilon_l < \epsilon_m$ is fulfilled⁵.

(3) Having chosen two transitions in this way, we either have $\beta_{0l} < \beta_{0m}$ or $\beta_{0l} > \beta_{0m}$. In the following we consider the first case⁶ and insert the definition of virtual

⁴Virtual temperatures are not defined between degenerate levels.

⁵Positivity of the energies is not crucial but a gauge convention which ensures it is assumed in the following (without loss of generality) in order to simplify the discussion.

⁶The proof for the second case is exactly analogous with reversed inequality signs (including in Equation (A.2) at the point where it is referred to below).

temperature, Equation (A.3):

$$\beta_{0l} < \beta_{0m} \quad (\text{A.5})$$

$$\frac{\log r_0 - \log r_l}{\epsilon_l - \epsilon_0} < \frac{\log r_0 - \log r_m}{\epsilon_m - \epsilon_0} \quad (\text{A.6})$$

$$\frac{a}{N} \frac{\epsilon_m - \epsilon_0}{\epsilon_l - \epsilon_0} < \frac{a}{N} \frac{\log r_0 - \log r_m}{\log r_0 - \log r_l} \quad (\text{A.7})$$

Now one can always find two natural numbers $a < N$ such that the left-hand side of Equation (A.7) is smaller than one while the right-hand side remains larger, hence violating the condition for complete passivity imposed by Equation (A.2). In other words, we may always find two N -partite levels, $E_a = a\epsilon_0 + (N-a)\epsilon_l$ and $E_b = N\epsilon_m$, which show population inversion for some possible choice of a and N . With this procedure, any given passive state π which is not thermal may be activated.

The same construction is not possible for a thermal state, where the virtual temperatures between all transitions are the same because Equation (A.5) does not hold for any transitions in that case. Even so, we still need to prove that thermal states cannot be activated (by some other procedure). This is done in the next paragraph by showing that $\tau_\beta^{\otimes N}$ is thermal (and hence passive) for any N .

First, however, we need to clarify the special case where $r_m = 0$ ⁷. In this case we may directly invoke Equation (2.12) and restate Equation (A.1):

$$a\epsilon_m + (N-a)\epsilon_0 < N\epsilon_l \Rightarrow r_m^a r_0^{N-a} \geq r_l^N. \quad (\text{A.8})$$

Choosing $a = 1$, the condition on the left may always be fulfilled for some N while the inequality on the right becomes $0 \geq r_l^N$ and can never be fulfilled for $r_l > 0$. Hence, the state may always be activated, as in the general case.

⁷The case of either r_0 or r_l vanishing is excluded by the remarks in footnote 2.

(4) It is straightforward to see, using multinomial expansion, that any combination of N identical thermal states is in turn thermal:

$$\begin{aligned}
\tau_\beta^{\otimes N} &= \frac{1}{Z^N} \left[\sum_k e^{-\beta \epsilon_k} |\epsilon_k\rangle\langle\epsilon_k| \right]^{\otimes N} \\
&= \frac{1}{Z^N} \sum_{\mathbf{m}} \exp\left[-\beta \sum_{k=1}^d m_k \epsilon_k\right] \sum_{\mu_m} |E_m, \mu_m\rangle\langle E_m, \mu_m| \\
&= \frac{1}{Z^{(N)}} \sum_{\mathbf{m}, \mu_m} e^{-\beta E_m} |E_m, \mu_m\rangle\langle E_m, \mu_m|,
\end{aligned} \tag{A.9}$$

where the first sum in the second line goes over all combinations $\mathbf{m}$ of m_k which sum to N : $\sum_{k=1}^d m_k = N$. d is the subsystem dimension. The states $|E_m, \mu_m\rangle$ correspond to the eigenenergies $E_m = \sum_{k=1}^d m_k \epsilon_k$ of the N -body Hamiltonian H_N . Each energy E_m is degenerate with a multiplicity equal to the multinomial coefficient⁸

$$\binom{N}{m_1, m_2, \dots, m_d} := \frac{N!}{m_1! m_2! \dots m_d!}, \tag{A.10}$$

and eigenstates in the degenerate subspaces are labelled by μ_m . It is easy to see that Equation (A.9) indeed represents a thermal state with $Z^{(N)} = Z^N$.

This concludes the proof that a passive state π is completely passive if and only if it is thermal.

⁸There may of course be additional degeneracies amongst different E_m depending on the eigenvalues $\{\epsilon_k\}$ of H . These are here accounted for as separate contributions to the sum.

Key concepts of quantum physics and quantum information theory

This appendix is included as a reference for some relevant concepts from quantum mechanics and quantum information theory. Its purpose is twofold: for one part, it may serve as a reference for the main chapters (i.e., for notation). Secondly, a doctoral thesis should be accessible to any physics graduate and this section includes those relevant elements of quantum theory which are not part of standard undergraduate syllabi. Since this is a pedagogical section and since the presented topics are basic canon in quantum theory, we omit references to individual results as well as proofs^a. Moreover, we choose to state results in only as much generality as is necessary for the present context rather than to overburden this appendix with more mathematical detail than is required for the main part of the thesis.

Quantum mechanics may largely be expressed in terms of linear algebra and inherits a significant part of its terminology. In this appendix, we assume that the reader is familiar with the basic notions of linear algebra.

^aBoth may be found in standard textbooks on quantum information theory – e.g. in the popular introduction by Nielsen and Chuang [2000], or in the (more mathematical) lecture notes by Watrous [2011] which are freely available online. A range of further, concise textbooks at the introductory level is also available – e.g. the books by Vedral [2006]; Schumacher and Westmoreland [2010]. The theory and formalism of open quantum systems, in particular master equations, are covered in great detail by Breuer and Petruccione [2002]. Wolf [2012] provides a useful lecture script on quantum operations on his website.

B.1 Quantum states

B.1.1 Hilbert space, (pure) states, and operators

The state space of quantum physics is Hilbert space¹ – a complete, complex vector space endowed with an inner product. In this thesis, we mostly think of discrete (and often also finite) Hilbert spaces. All expressions in this section may be extended to continuous Hilbert spaces but are here expressed for the discrete case.

A so-called *pure* quantum state $|\psi\rangle$ is represented by a unit-length vector on the quantum system’s Hilbert space and is here denoted by a Dirac *ket*. It contains all information that could be known about the system.

A linear mapping between two Hilbert spaces, $O : \mathcal{H}_1 \rightarrow \mathcal{H}_2$, is called an *operator*. It may be expressed in terms of elements of the Hilbert space and its dual, the latter being expressed by Dirac *bras*: for instance, the dual vector to $|\psi\rangle$ is written as $\langle\psi|$. We here only consider operators which map onto the same space (i.e., $\mathcal{H}_1 = \mathcal{H}_2$ in the above expression).

¹More precisely, we might say *projective* Hilbert space in order to emphasize that the global phase of a quantum state has no physical significance.

Observables – that is, all physical quantities which can in principle be measured – are represented by self-adjoint (or, synonymously, Hermitian) operators². A Hermitian operator's eigenvalues are always real and represent the possible measurement outcomes corresponding to the observable. Any Hermitian operator O may be written in diagonal form (i.e., in terms of its eigenvalues O_n and eigenstates $|o_n\rangle$) as

$$O = \sum_n O_n |o_n\rangle\langle o_n|. \quad (\text{B.1})$$

Conversely, any orthonormal base $\{|o_n\rangle\}$ defines a family of Hermitian operators (with different eigenvalues). Equation (B.1) is called *spectral decomposition* of O and the set of O_n is called the *spectrum* of O . The equation may be used to define functions of Hermitian operators as

$$f(O) := \sum_n f(O_n) |o_n\rangle\langle o_n|, \quad (\text{B.2})$$

where f is directly applied to the eigenvalues of the operator O .

B.1.2 The density operator formalism and mixed states

In general, it may happen that the (pure) state of a system is not precisely known. This lack of knowledge may be fundamental (i.e., due to quantum correlations with another system) or of a more practical origin (e.g., due to imprecise state preparation in the laboratory). In either case, the quantum state cannot be described by a pure state and a more general formalism is required. To this end the density operator

$$\rho := \sum_n p_n |\psi_n\rangle\langle\psi_n| \quad (\text{B.3})$$

²In line with customary convention, we denote the Hermitian conjugate of an operator O by a ‘dagger’ as $O^\dagger$.

may be introduced. Here, p_n is the probability of the system being in state $|\psi_n\rangle$. The probabilities sum to one: $\sum_n p_n = 1$. States described by a density operator are called *mixed* states³. For a mixed state ρ , we define its *purity* as

$$\mathcal{P}(\rho) := \text{tr}[\rho^2]. \quad (\text{B.4})$$

Just like any quantum operator, the density operator of a state ρ may be expressed in any orthonormal basis $\{|m\rangle\}$ ⁴:

$$\rho = \sum_{m,n} \rho_{m,n} |m\rangle\langle n|. \quad (\text{B.5})$$

In a given basis, the diagonal entries $\rho_{m,m}$ are called *populations* and the off-diagonal elements are called *coherences*. We emphasise that the appearance of coherences is always contingent on the basis and it is always possible to find a diagonal matrix representation for ρ (i.e., Equation (B.1)). As for any operator, the entries of the diagonal representation (the eigenvalues of ρ) are collectively called its *spectrum*. For density matrices,

$$0 \leq \rho_{n,n} \leq 1, \text{ and} \quad (\text{B.6})$$

$$\text{tr}[\rho] = 1 \quad (\text{B.7})$$

for all n and any orthonormal basis $\{|n\rangle\}$.

B.1.3 Qubits

A quantum system with a two-dimensional Hilbert space (spanned by some orthonormal basis $\{|0\rangle, |1\rangle\}$) is called a quantum bit, or *qubit*. Its state may be represented

³We here adopt the common convention that understands pure states as a subset of mixed states. We call states that are not pure *non-pure*.

⁴We label all three, the state, its density operator, and the matrix $\rho_{m,n}$, as ρ .

in terms of the *Pauli operators*

$$\sigma_x := |1\rangle\langle 0| + |0\rangle\langle 1|, \quad (\text{B.8})$$

$$\sigma_y := i|1\rangle\langle 0| - i|0\rangle\langle 1|, \quad (\text{B.9})$$

$$\sigma_z := |0\rangle\langle 0| - |1\rangle\langle 1|, \quad (\text{B.10})$$

and the identity operator $\mathbf{I}_2 = |0\rangle\langle 0| + |1\rangle\langle 1|$ as

$$\rho = \frac{1}{2} (\mathbf{I}_2 + r \sin \theta \cos \phi \sigma_x + r \sin \theta \sin \phi \sigma_y + r \cos \theta \sigma_z). \quad (\text{B.11})$$

This parametrisation allows for the representation of a qubit state on a sphere of unit radius called *Bloch sphere*. In this representation, $0 \leq r \leq 1$ is the distance from the coordinate origin, and θ and ϕ are the zenith and azimuth angle, respectively.

B.1.4 (Projective) measurement

When an observable O is to be measured, the possible measurement outcomes are its eigenvalues O_n . For a system in a state ρ , the probability of obtaining measurement outcome O_n is given by

$$p(O_n) = \langle o_n | \rho | o_n \rangle, \quad (\text{B.12})$$

or, equivalently, by the element $\rho_{n,n}$ of the state's density matrix representation in the basis $\{|o_n\rangle\}$. Right after obtaining measurement outcome O_n , the system is found in state $|o_n\rangle$ with certainty.

The *expectation value* $\langle O \rangle$ of the observable O may be computed according to the standard definition:

$$\langle O \rangle = \sum_n p(O_n) O_n \quad (\text{B.13})$$

$$= \sum_n \langle o_n | \rho | o_n \rangle O_n \quad (\text{B.14})$$

$$= \text{tr}[\rho O]. \quad (\text{B.15})$$

This type of measurement is called *projective* measurement⁵.

B.1.5 Composite systems

A quantum system may consist of more than one subsystem. Its state then belongs to the tensor product Hilbert space

$$\mathcal{H} = \bigotimes_n \mathcal{H}_n, \quad (\text{B.16})$$

where n labels each individual subsystem.

If the individual subsystem states are completely independent from each other – that is, not correlated – their composition, the global state ρ , is a *product state*:

$$\rho = \bigotimes_n \rho_n. \quad (\text{B.17})$$

If the total state is not a product state but may be written in the form

$$\rho = \sum_n p_n \bigotimes_n \rho_n \quad (\text{B.18})$$

⁵There are in fact more general types of quantum measurement but we leave those to the textbooks since they are not of relevance for this thesis.

it possess classical correlations and we call such states *separable*. All other states which cannot be written in the form of Equation (B.18) carry quantum correlations and are hence called *entangled*.

Given a global (generally entangled) state ρ a local state ρ_j is expressed derived by taking the *partial trace* over all other subsystems in ρ

$$\rho_j := \text{tr}_{k \neq j}[\rho] := \sum_l \langle b_l | \rho | b_l \rangle. \quad (\text{B.19})$$

Here, $\{|b_l\rangle\}$ is some orthonormal basis for all subsystems other than j .

Due to entanglement, even a pure state $\rho = |\psi\rangle\langle\psi|$ will be non-pure locally, thus motivating the density operator formalism from a fundamental perspective. An ignorance of the state may hence be due to experimental reasons and lack of precision as much a quantum correlations which forbid precise knowledge of the local state *in principle*.

An adequate measure of the ‘ignorance’ about a quantum state ρ is given by the *von Neumann entropy*

$$S(\rho) := -\text{tr}[\rho \log \rho]. \quad (\text{B.20})$$

B.2 Quantum evolution

B.2.1 Unitary evolution

The evolution of a quantum state is governed by the time-dependent Schrödinger equation⁶:

$$i\hbar \frac{d}{dt} |\psi\rangle = K(t) |\psi\rangle. \quad (\text{B.21})$$

⁶In this appendix, $\hbar$ -dependence is made explicit even though the rest of this thesis (apart from Box 3.1) adopts the convention $\hbar = 1$.

It gives rise to the evolution operator

$$U(t, t_0) := T_{\leftarrow} \exp \left[-\frac{i}{\hbar} \int_{t_0}^t K(s) ds \right], \quad (\text{B.22})$$

where the time-ordering operator $T_{\leftarrow}$ ensures that later times in the integral get multiplied from the left. We generally simplify notation by setting $t_0 = 0$ and writing $U_t := U(t, t_0 = 0)$, or even U without explicit time-dependence in situations where unitarity of the evolution (i.e., $U^\dagger U = \mathbf{I}$) but not its specifics are of relevance. Using Equation (B.22), an initial state $|\psi\rangle$ evolves into a state

$$|\psi'_T\rangle := U_T |\psi\rangle \quad (\text{B.23})$$

after a time T . In the same way, a mixed state ρ evolves to

$$\rho'_T = U_T \rho U_T^\dagger. \quad (\text{B.24})$$

The same unitary evolution which is expressed by Equation (B.22) may also be written in infinitesimal form in the *Liouville-von Neumann equation*:

$$\dot{\rho} := \frac{1}{i\hbar} [K(t), \rho], \quad (\text{B.25})$$

where the dot above ρ indicates the time-derivative as elsewhere in this thesis. For a given driving $K(t)$ Equations (B.21) and (B.25) both fully specify the unitary evolution of an initial state ρ .

B.2.2 Local operations and classical communication (LOCC)

The class of separable states introduced above may be related to a class of operations which keep any separable state separable. This class of operations is known as

LOCC. It consists of all compositions of evolutions that are local (that is, effecting each subsystem separately). All non-LOCC operations induce entanglement on some initially separable state(s).

In this sense, quantum entanglement has long been understood as a resource which may only be created by non-LOCC operations.

B.2.3 Completely-positive and trace-preserving (CPTP) maps

CPTP maps, synonymously called *quantum operations* or *quantum channels*⁷, are a type of mapping from a space of density operators onto another⁸. They are those linear maps M which may be represented by *Kraus operators* K_j as

$$M(\rho) = \sum_j K_j \rho K_j^\dagger, \quad (\text{B.26})$$

for any input state ρ . Here, the requirement

$$\sum_j K_j^\dagger K_j = \mathbf{I} \quad (\text{B.27})$$

ensures that the output state $\rho' := M(\rho)$ has unit trace⁹:

$$\text{tr}[\rho'] = \text{tr} \left[\sum_j K_j \rho K_j^\dagger \right] = \text{tr} \left[\rho \sum_j K_j^\dagger K_j \right] = \text{tr}[\rho] = 1. \quad (\text{B.28})$$

The second equality in this equation follows from cyclicity of the trace, i.e., $\text{tr}[AB] = \text{tr}[BA]$.

⁷Sometimes, quantum channels and quantum operations are distinguished by the former being strictly trace-preserving, while the latter need not fulfil this property. We here ignore that subtle difference and only focus on trace-preserving maps.

⁸There is no general requirement that the output space be the same as the input space: i.e., the dimension may change. In this thesis, however, we assume that both spaces are the same.

⁹Maps which fulfil the condition $\sum_j K_j K_j^\dagger = \mathbf{I}$ are called *unital*.

CPTP maps arise as a natural description of the evolution of an open system. Consider a (primary) system that starts in a state ρ and an ancillary system (or simply: an *ancilla*) which starts in a pure state $|\phi\rangle$. Both systems evolve together unitarily and then the primary system is regarded on its own. It has evolved to the output state

$$\rho' = \text{tr}_A [U \rho \otimes |\phi\rangle\langle\phi| U^\dagger], \quad (\text{B.29})$$

where tr_A indicates a partial trace over the ancilla. Choosing an orthonormal basis $\{|a_n\rangle\}$ of the ancilla system we may make the following identification:

$$K_j := \langle a_j | U | \phi \rangle. \quad (\text{B.30})$$

The evolution of the system of interest may hence be described by a CPTP map.

Conversely, it can be shown that for any CPTP map M , acting on a d -dimensional system, some ancilla system of at most dimension d^2 and some unitary U can be found such that Equations (B.26) and (B.30) describe the action of the map for all input states ρ . This is called *Stinespring dilation*.

The Kraus operators introduced in this section generally carry the time dependence of the generating unitary, according to Equations (B.22) and (B.30). They hence define a family of maps $M(t, t_0)$ and, consequently, a time-dependent output state $\rho'(t, t_0)$. In general, however $M(T)$ need not be decomposable: the decomposition $M(t, t_0) = M(t, t')M(t', t_0)$ need not exist for all times t' . In fact, $M(t, t_0)$, and hence $\rho(t, t_0)$ may not be defined for all times t .

B.2.4 Master equations

In practice, it is often desirable to obtain an expression like Equation (B.25) which specifies the time-derivative $\dot{\rho}$ of the reduced system state. Such equations are called *master equations*.

A particular (but, nonetheless, general) type of master equation, the *Gorini-Kossakowski-Sudarshan-Lindblad master equation*¹⁰, may be expressed as

$$\dot{\rho} = \frac{1}{i\hbar} [\tilde{K}(t), \rho] + \sum_{j=1}^{d^2-1} \gamma_j \left(A_j \rho A_j^\dagger - \frac{1}{2} [\rho, A_j^\dagger A_j] \right). \quad (\text{B.31})$$

Here, the *Lindblad operators* A_j span the space of operators acting on the system's Hilbert space. For a system of dimension d , the space of operators acting on it – itself a Hilbert space called *Hilbert-Schmidt* space – is of dimension N^2 and may always include the identity operator as one basis element. The rates γ_j may be explicitly calculated for a specific evolution due to a global Hamiltonian acting on both system and ancilla (with weak coupling between them). In practice, when the ancilla is an *environment*¹¹ whose precise details are unknown, the rates may be determined experimentally.

Importantly, $\tilde{K}(t)$ – the Hermitian contribution of the open system dynamics – is not generally the thermodynamically meaningful reference Hamiltonian. More specifically, given some splitting of the global Hamiltonian into a system, ancilla, and interaction part as $K_{tot} = K_S + K_A + K_I$ – one of the key steps in deriving Equation (B.31) – in general, $\tilde{K} \neq K_S$.

Equation (B.31) relies on a number of fundamental approximations and assumptions about the system and its dynamics – most crucially, the *Born-Markov approximation* which requires system and ancilla to be initially uncorrelated and weakly coupled. In addition, the approximation assumes that environmental correlations vanish on a faster time-scale than that of the system dynamics.

¹⁰The equation is more commonly simply referred to as *Lindblad equation* and sometimes also as *Kossakowski-Lindblad master equation*.

¹¹We differentiate between the notion of an ancilla, whose dynamics and details are known and potentially even controllable, and an environment of which only the effect on the system is known.

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