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On the energetic analysis of autonomous quantum systems

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This thesis is dedicated to all people who work hard against misinformation
and to developing science in Brazil.
Most importantly, it is dedicated to all, direct and indirect, victims of this pandemic.

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"The unexamined life is not worth living."

Socrates

ABSTRACT

MALAVAZI, A. H. A. **On the energetic analysis of autonomous quantum systems**. 2022. 135p. Thesis (Doctor in Science) - Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, 2022.

During the last decades, there have been many theoretical and experimental advances both in the extension of thermodynamics to comprise microscopic systems out-of-equilibrium and in the understanding of quantum mechanics. Along with the state-of-the-art capability of controlling fragile quantum systems in a wide variety of physical platforms, this context has paved the way for the current strategic efforts to develop a thermodynamic theory of quantum systems. In this sense, the research field coined as quantum thermodynamics (QT) already plays a key role in the design and development of future quantum-based technologies. More specifically, QT aims both to apply the usual thermodynamic concepts and notions to describe arbitrary non-equilibrium quantum systems and to understand the emergence of classical thermodynamic behaviour from the underlying fundamentally quantum dynamics. However, despite all current progress, there is still no consolidated formalism for a general thermodynamic description of fully autonomous quantum objects. Besides, the lack of consensus on some central aspects, such as the definitions of quantum counterparts of thermodynamic quantities, is particularly notorious. In this thesis, we focus on the energetic analysis within autonomous quantum systems. To this aim, we propose a novel and general formalism for a dynamic description of the energy exchanges between interacting subsystems. From the Schmidt decomposition approach, we identify effective Hamiltonians as the representative operators for characterizing the local internal energies, whose expectation values satisfy the usual thermodynamic notion of energy additivity. In contrast to the currently used methodologies, such procedure treats the subsystems with equal footing and do not rely on any sort of approximations and additional hypotheses, e.g., semi-classical description, weak-coupling regime, strict energy conservation and Markovian dynamics. In short, our proposal contributes to the development of QT by providing a new formalism that does not suffer from the usual restrictive shortcomings and establishes a new and exact route for defining other general thermodynamic quantities to the quantum regime.

Keywords: Quantum thermodynamics. Open quantum systems.

RESUMO

MALAVAZI, A. H. A. **Sobre a análise energética de sistemas quânticos autônomos**. 2022. 135p. Tese (Doutorado em Ciências) - Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, 2022.

Durante as últimas décadas, houve muitos avanços teóricos e experimentais tanto na extensão da termodinâmica para abranger sistemas microscópicos fora de equilíbrio quanto na compreensão da mecânica quântica. Somada a capacidade de última geração de controlar sistemas quânticos frágeis em uma ampla variedade de plataformas físicas, esse contexto abriu caminho para os atuais esforços estratégicos para desenvolver uma teoria termodinâmica de sistemas quânticos. Nesse sentido, o campo de pesquisa cunhado como termodinâmica quântica (TQ) já desempenha um papel fundamental no projeto e desenvolvimento de futuras tecnologias baseadas em fenômenos quânticos. Mais especificamente, a TQ visa tanto aplicar os conceitos e as noções termodinâmicas usuais para descrever sistemas quânticos arbitrários fora do equilíbrio quanto entender o surgimento do comportamento termodinâmico clássico a partir da dinâmica fundamentalmente quântica subjacente. No entanto, apesar de todo o progresso atual, ainda não existe um formalismo consolidado para uma descrição termodinâmica geral de objetos quânticos totalmente autônomos. Além disso, é particularmente notória a falta de consenso em relação a alguns aspectos centrais, como as definições de análogos quânticos de grandezas termodinâmicas. Nesta tese, focamos na análise energética em sistemas quânticos autônomos. Para isso, propomos um novo formalismo geral para uma descrição dinâmica das trocas energéticas entre subsistemas interagentes. A partir da abordagem da decomposição de Schmidt, identificamos Hamiltonianos efetivos como os operadores representativos para caracterização das energias internas locais, cujos valores esperados satisfazem a noção termodinâmica usual da aditividade de energia. Ao contrário das metodologias atualmente utilizadas, tal procedimento trata os subsistemas em pé de igualdade e não depende de nenhum tipo de aproximações e hipóteses adicionais, por exemplo, descrição semiclássica, regime de acoplamento fraco, conservação de energia estrita e dinâmica Markoviana. Em suma, nossa proposta contribui para o desenvolvimento da TQ fornecendo um novo formalismo que não sofre das restrições usuais e estabelece uma nova e exata rota para definir outras grandezas termodinâmicas gerais para o regime quântico.

Palavras-chave: Termodinâmica quântica. Sistemas quânticos abertos.

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1 INTRODUCTION

Quantum thermodynamics is a rapidly growing and promising field of research, accumulating efforts from several distinct perspectives. Its flourishing is inextricably linked to recent technological advances and current independent theoretical progress in the fields of nonequilibrium thermodynamics and quantum mechanics. On the one hand, state-of-the-art experiments allow the precise control of small, and possibly quantum, systems in several platforms. On the other, yet the laws of thermodynamics have been successfully verified to microscopic scales when considering ensemble realizations of the experiment, and studies on quantum information elucidated the technological potential of harnessing genuine quantum phenomena. However, the task of developing a consistent and somehow meaningful thermodynamic theory of quantum systems proved to be non-trivial and far from being straightforward. In this sense, the most current approaches are restricted to specific scenarios of approximative descriptions and semi-classical treatments, i.e., it is commonly assumed externally driven systems (by means of classical agents), weak-coupling regime and Markovian dynamics. Along these lines, there is no unifying formalism for characterizing the thermodynamics *within* general autonomous quantum systems, and many fundamental open questions remain unanswered. Remarkably, it is unclear how to define quantum counterparts of the most basic thermodynamic quantities. This context highlights the importance of further research, especially on conceptual aspects of the theory. The work in question falls within this scope[a].

This thesis is organized as follows: Chapter (2) contextualizes the field of quantum thermodynamics. It initially introduces the basic concepts and formalism of thermodynamics and quantum mechanics separately. Then it provides a brief overview of quantum thermodynamics and discusses its current status and open problems; Chapter (3) contains the main sections of the thesis. It develops and proposes a novel framework for analyzing the energetics within autonomous pure bipartite quantum systems. This proposal is exact, symmetrical and based on a well-established mathematical tool: the Schmidt decomposition procedure. More specifically, it introduces time-dependent local effective Hamiltonians interpreted as the representative operators for characterizing the physical local internal energies. This identification allows the description of the subsystems effective dynamics within general interacting subsystems, regardless of their particular properties and coupling regimes, and also recovers the usual thermodynamic property of energy additivity. Besides, it briefly discusses the current approaches and difficulties for defining general quantum versions of core thermodynamic quantities. After that, the

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[a] The main discussions and results introduced in this thesis were presented in (1) after its defense.

introduced formalism is extended for mixed states; Finally, the conclusions of this thesis are addressed in Chapter (4). It summarizes its main messages and provides a perspective for future work considering the general context of quantum thermodynamics.

2 CONTEXTUALIZATION

This chapter aims to contextualize the field of research in which this work is inserted, known as *quantum thermodynamics*. To this end, a brief detour is necessary to introduce its main ingredients, namely *thermodynamics* and *quantum mechanics*. Of course, this is not an extensive review of both areas. Instead, these notes intend to provide an overview of the context and main motivations for the development of a thermodynamic theory of quantum systems.

In this sense, Section (2.1) presents the basic concepts of classical equilibrium thermodynamics and the recently established research area of stochastic thermodynamics. Then, Section (2.2) discusses the formalism of quantum mechanics. Finally, Section (2.3) formally introduces quantum thermodynamics and its current status.

2.1 Thermodynamics

Thermodynamics is, undoubtedly, one of the most successful physical theories in the history of science. It is no overstating to say that the foundations of modern society were significantly influenced by the technological innovations brought by it. Its range of predictions and applicability is surprisingly far-reaching, especially if considering its restrictions and the circumstances of its developments. In this sense, all branches of modern science and engineering function accordingly to the laws of thermodynamics. Nevertheless, even after centuries of discussions, its results and statements continue to inspire and instigate novel research and surprising connections.

Despite earlier developments, the theory of thermodynamics was born during the 17th century and flourished as an influential branch of physics during the 18th and 19th centuries[a]. Since its early days, thermodynamics was developed as a phenomenological discipline and approached semi-empirically. It initially progressed through scientists' efforts to understand better the behaviour of gases and the "abhors" nature of the vacuum[b]. Then, it proceeded as a fundamental way to characterize different aspects of energy exchange through work and heat, along with the notions of irreversibility and entropy. As often happens in science, these investigations were partially motivated by the technological advancements of the time: the development of new instruments, such as vacuum pumps, the thermometer and steam engines, provided the necessary means to perform novel and better measurements and push even further the progress of the theory. Surprisingly, this context also triggered the unprecedented technological transformation that led western society toward the Industrial Revolution and, eventually, the thriving of mod-

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[a] For a historical perspective on the development of thermodynamics, see. (2)

[b] "*Natura abhorret vacuum*"

ern machinery. In fact, the progress of thermodynamics was driven considerably by the attempts to understand and develop efficient machines. In this sense, despite the pragmatical and sober motivation, it is remarkable how these studies guided scientists toward the establishment of general and fundamental laws of nature.

Seeing from the privilege of modern science, the phenomenological approach to thermodynamics could hardly have been different. The microscopic behaviour of matter remained hidden from scientists' eyes for a long time, and the tools of analytical mechanics, along with its mechanistic view of nature, were being developed in parallel to thermodynamics. In this sense, its history is also intrinsically connected to the concomitant developments of chemistry and classical mechanics. Along these lines, at that time, the empirical observation that mass[c], momentum and energy were conserved quantities in isolated systems was still under scrutiny and far from consensus. In fact, even these individual notions - including "isolated systems" - were not entirely established. Heat, for instance, was not directly associated with the mechanical motions of particles or the "vis viva", the earlier version of kinetic energy, until the efforts of Joule, when he established the relationship between energy, work and heat. Instead, the orthodox explanation was given by the so-called caloric theory. Interestingly, this was also the context for the development of heat engines and the theoretical studies concerning their performances, which set the stage for the works of Sadi Carnot (1796 - 1832) - and later Rudolf Clausius (1822 - 1888) - on what we know today as the second law of thermodynamics and the concept of entropy.

After that, names like James Clerk Maxwell (1831 - 1879), Ludwig Boltzmann (1844 - 1906) and Josiah Willard Gibbs (1839 - 1903) were responsible for providing the microscopic and mechanical basis of phenomenological equilibrium thermodynamics. Such progress is depicted by the kinetic theory of gases and the following foundation of statistical mechanics. Most importantly, these developments represent a crucial paradigm shift concerning the understanding of the macroscopic nature, i.e., the introduction of probabilistic reasoning and thermodynamic ensembles provided the necessary tools for - at least partially - bridging the gap between the underlying microscopic motion and the observed macroscopic behaviour. More recently, during the 20th century, physicists, such as Lars Onsager (1903 - 1976) and Ilya Prigogine (1917 - 2003), began to extrapolate thermodynamics to the uncharted territory of non-equilibrium regimes. After all, most natural processes occur under these conditions. Along these lines, the analysis of systems close to equilibrium, known as the linear regime, provided the formalism for investigating several physical phenomena and represented the starting point of the characterization of non-equilibrium states.

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[c] Strictly speaking, mass does not conserve due to the mass-energy equivalence. However, in the present thermodynamic context, this difference is negligible.

As mentioned earlier, thermodynamics has still been an active field of research. During the last decades, one can find great efforts to extend the theory and its results to even broader scenarios, namely microscopic and far-from-equilibrium settings. In such regimes, thermal fluctuations play a critical role in the dynamics of the desired physical system, and the usual thermodynamic quantities are updated to random variables. In this sense, stochastic thermodynamics and its fluctuation theorems have been providing seminal results concerning non-equilibrium processes and irreversibility.

2.1.1 Classical equilibrium thermodynamics

Let us briefly present and review the classical equilibrium thermodynamics and its main statements. Of course, there are several traditional textbooks written on the subject. For a comprehensive discussion of thermodynamics see. (3–7)

Classical thermodynamics restricts itself to a specific, though meaningful, physical regime and scope. Essentially, it was developed to describe the behaviour of large scale properties of classical *macroscopic* objects and their general relationships. Since it is a phenomenological description, it does not require any microscopic consideration concerning the structure of matter. Instead, it provides a macroscopic and fully general characterization in terms of a few measurable gross variables $\{X_j\}$, known as thermodynamic coordinates, such as volume (V), pressure (P) and temperature (T). In this sense, once obtained the relevant coordinates for describing a system, one has specified its physical state and, along with it, has access to all thermodynamic properties that are functions of it, referred to as state functions, i.e., $F(\{X_j\})$. Such a procedure is only possible because classical thermodynamics revolves around the concept of states in *thermodynamic equilibrium.* These states are characterized by their static, or time-invariant, nature, such that all possible thermodynamic coordinates remain fixed[d]. In contrast, non-equilibrium states might not even have specified values for them. It is an empirical fact that many physical systems naturally (spontaneously) evolve in time from non-equilibrium states towards these constant states. It is worth mentioning that everything that happens during this dynamic process is outside the scope of classical equilibrium thermodynamics.

Along these lines, it is also possible to define a succession of changes connecting different equilibrium states, which establishes a *thermodynamic process.* If the initial and final states are the same, the whole process is known as a thermodynamic cycle, which represents the building blocks of any heat engine. Visually, thermodynamic processes and cycles are usually depicted by trajectories in the space of equilibrium states defined in terms of the thermodynamic coordinates $\{X_j\}$. Of course, any change presupposes some degree of variation of a macroscopic variable that, in general, would perturb the system

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[d] One can also refer to equilibrium states relative to specific macroscopic coordinates, such as mechanical, chemical and thermal.

and kick it out of equilibrium until it reaches a novel one in terms of the new setting. Nevertheless, as long as the changes are kept infinitesimal, the system is weakly perturbed and maintained close to equilibrium. Such a convenient condition characterizes a so-called *quasi-static process*. Notice that any ideal thermodynamic process would require an infinite amount of time to be performed. However, in many realistic scenarios, this theoretical abstraction represents a satisfactory approximation. Interestingly, the rate of processes is not addressed by classical equilibrium thermodynamics, which highlights that the theory is not a truly dynamic one, at least not in the usual sense.

2.1.1.1 The laws of thermodynamics

The physical object under scrutiny, or the thermodynamics system, is usually classified according to the ways it interacts with its exterior, especially concerning the possibility of exchanging matter or energy with its surroundings. In this sense, isolated systems, as the name suggests, do not interact with other objects and, therefore, exchange neither things. Closed systems only exchange energy, while open systems exchange both energy and matter. Naturally, these interactions are accompanied by thermodynamic processes, both from the system and its surroundings. The possible state transformations are described, and constrained, by a set of empirical and mathematical statements known as the *laws of thermodynamics*. Let us now briefly introduce them.

2.1.1.1.1 Zeroth law of thermodynamics

As mentioned earlier, thermodynamic systems eventually reach equilibrium states. It implies that if two independent systems are allowed to interact, the single entity constituted by both individuals will also equilibrate. Thus, it is an experimental fact that interacting bodies that are specified by distinct temperatures will reach thermal equilibrium. Along these lines, if systems A and B are individually in thermal equilibrium with system C, then A and B are also in equilibrium. Such transitivity property is known as the *zeroth law of thermodynamics*.

2.1.1.1.2 First law of thermodynamics

Essentially, the first law of thermodynamics refers to the conservation of energy within thermodynamic systems. However, instead of being written in terms of the sum of all the kinetic and potential contributions of its microscopic constituents, the internal energy relative to state k, U_k, is a state function specified by the relevant macroscopic variables $\{X_j^k\}$, i.e.,

$$U_k \equiv U(\{X_j^k\}) + U_0, \tag{2.1}$$

where U_0 is the energy of a reference state. Notice that it means that the internal energy change $U_b - U_a$ from a state a to b is independent of the thermodynamic process, γ, connecting them, such that

$$\int_{\gamma} dU = \int_{\gamma'} dU = U_b - U_a, \tag{2.2}$$

where dU is an exact differential, and

$$\oint dU = 0 \tag{2.3}$$

for any cyclic transformation.

It is clear that isolated system, by construction, maintains its internal energy fixed since any energetic change requires the system to be submitted to a thermodynamic process. Thus, let us now consider closed systems. Thermodynamics, and the first law specifically, not only state energy conservation but also splits its possible changes into two different "flavours": heat, Q, is the type of energy exchanged once systems of different temperatures are interacting or, as commonly said, put into thermal contact; work, W, in contrast, is the energy transferred (not stochastically) by the external change of the thermodynamic coordinates. Along these lines, in the simplest scenario consisting of two interacting bodies reaching thermal equilibrium, the energetic exchange of the system under consideration is completely due to heat, or

$$\Delta U = Q. \tag{2.4}$$

However, for a thermally insulated system, one can perform work and modify the system's state simply by externally controlling its macroscopic variables, such that

$$\Delta U = W. \tag{2.5}$$

This kind of procedure where no heat is involved, is characterized as an adiabatic process. Nevertheless, considering general interactions, both contributions might be present for arbitrary processes. Thus, for an infinitesimal energy change, dU, the *first law of thermodynamics* is stated as

$$dU \equiv \delta Q + \delta W, \tag{2.6}$$

where δW and δQ are the infinitesimal work performed on the system and the heat transferred into it, respectively. In contrast with internal energy, both individual quantities are not state functions. Instead, they are intrinsic to thermodynamic processes. Such path dependency is mathematically represented by the inexact differentials δW and δQ. Thus, given two possible trajectories, γ and γ', connecting different states a and b, we have

$$W_\gamma \equiv \int_{\gamma} \delta W \neq \int_{\gamma'} \delta W \equiv W_{\gamma'}, \tag{2.7}$$

$$Q_\gamma \equiv \int_{\gamma} \delta Q \neq \int_{\gamma'} \delta Q \equiv Q_{\gamma'}, \tag{2.8}$$

even though

$$U_b - U_a = W_\gamma + Q_\gamma = W_{\gamma'} + Q_{\gamma'}. \tag{2.9}$$

It is worth mentioning that, for open systems, one just must consider an additional term dU_{matter} for the energy flow due to matter exchange.

2.1.1.1.3 Second law of thermodynamics

Interestingly, there are several distinct, though ultimately equivalent, ways for formulating the second law of thermodynamics. In this sense, according to Lord Kelvin (William Thomson, 1824 - 1907) (3):

> "*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.*"

On the same matter, Max Planck (1858 - 1947) wrote:

> "*It is impossible to construct an engine which, working in a complete cycle, will produce no effect other than the raising of a weight and the cooling of a heat reservoir.*"

However, both statements above are often combined into the so-called Kelvin-Planck statement of the second law:

> "*It is impossible to construct an engine that, operating in a cycle, will produce no effect other than the extraction of heat from a reservoir and the performance of an equivalent amount of work.*"

Also, in the words of Clausius:

> "*It is impossible to construct a device that, operating in a cycle, will produce no effect other than the transference of heat from a cooler to a hotter body.*"

Finally, Carnot's theorem states:

> "*No heat engine operating between two heat reservoirs can be more efficient than a reversible heat engine operating between the same two reservoirs.*"

Thus, according to these words, the second law of thermodynamics is a statement of what is impossible to achieve in the attempt of interchanging heat and work. However, these statements transcend the context of heat engines and refrigerators and have surprisingly far-reaching and less down-to-earth consequences. Essentially, the second law captures a fundamental feature of natural phenomena not covered by the first law, i.e., there are classes of processes not prohibitive from the perspective of the conservation of energy that still does not happen in nature. In this sense, the second law is an independent and complementary statement that also portrays a fundamental natural restriction. Moreover, it constrains even further the set of possible thermodynamic processes.

At the core of the second law also lies the concepts of reversibility and irreversibility. Suppose a thermodynamic system that interacts with its surroundings. Naturally, both work and heat may be exchanged during any change of the macroscopic variables. Nevertheless, a reversible process is, by definition, a process that, once realized, the system and its surroundings must be returned to their previous states, without any other change, by restoring the settings to their initial conditions. However, this is only achievable - a priori - by requiring processes executed by slow infinitesimal transformations (quasi-statically)[e] and in the absence of dissipative effects, such as friction. Along these lines, it is clear that reversible processes are theoretical idealizations and, consequently, every natural process occurs in a finite time and is irreversible to some extent.

Along with (ir)reversibility, entropy is a cornerstone of the second law. By introducing it, Clausius provided the means for a consistent mathematical formulation of the previous statements. Interestingly, the notion of entropy transcended thermodynamics and soon achieved the status of one of the most fundamental quantities of modern physics. As a direct extension of the work of Carnot on heat engines and cyclic thermodynamic processes (8), Clausius showed what we know today as Clausius's theorem (9),

$$\oint \frac{\delta Q}{T} = 0, \tag{2.10}$$

where T is the temperature at which the heat exchange took place[f]. Eq. (2.10) is valid for arbitrary cyclic and reversible processes and also hints at the existence of a state function specified by the macroscopic variables $\{X_j\}$, i.e., $\frac{\delta Q}{T}$ which depends only on the thermodynamic coordinates and its integral between two different states a and b is independent of the path (similar to Eq. (2.3)). Thus, Clausius proposed a new quantity S and named it *entropy*[g], such that

$$dS \equiv \frac{\delta Q}{T} \tag{2.11}$$

and, therefore, the entropic change is

$$\Delta S \equiv S_b - S_a = \int_a^b \frac{\delta Q}{T}. \tag{2.12}$$

Notice that, despite δQ being a path-dependent quantity, the ratio $\frac{\delta Q}{T}$ is an exact differential, dS. It is imperative to highlight both the close relationship between entropy and heat and the importance of the reversibility hypotheses. Let us suppose a system of interest interacting with a reservoir at temperature T. During any reversible process the heat exchanged, Q, between the system and reservoir happens at the same temperature,

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[e] In fact, every reversible process is necessarily quasi-static, while the converse is not true.

[f] This equality is obtained by noticing that any thermodynamic cycle can be seen as a composition of infinitesimal Carnot cycles and summing up all the ratios $\frac{Q_i}{T_i}$.

[g] Entropy means *transformation*, from the Greek word $\tau\rho\pi\eta$. (7)

in such a way that their local entropic changes are the opposite, i.e.,

$$\Delta S_{system} = -\Delta S_{reservoir}. \tag{2.13}$$

The equality above is true for every reversible process and sketches an even more general result: The sum of the entropies of the system of interest and all its surroundings, also known as the *universe*[h], is invariant over reversible processes, i.e., given $S_{universe} \equiv S_{system} + S_{surroundings}$, we have

$$\Delta S_{universe} = 0. \tag{2.14}$$

Of course, as mentioned earlier, reversible processes do not represent the typical behaviour in nature. Since entropy is a state function, given a system at equilibrium, any possible cyclic process, reversible or not, would still satisfy $\oint dS_{system} = 0$. However, if any irreversibility is taken into account, such as friction and other dissipative effects, Eq. (2.10) should be updated to the following inequality

$$\oint \frac{\delta Q}{T} \leq 0, \tag{2.15}$$

which also implies that

$$dS_{system} \geq \frac{\delta Q}{T}. \tag{2.16}$$

Besides, in these cases, the entropic change from the system of interest is not completely compensated by the changes that occur in the surroundings. In fact, in general, one has for the *second law of thermodynamics*

$$\Delta S_{universe} \geq 0. \tag{2.17}$$

Clearly, these expressions automatically include the previous ones: if no irreversible processes take place, then the equalities are recovered. Eq. (2.17) above is the most common mathematical statement of the second law: the entropy of the universe always increases or remains constant. It is also directly related to the notion of the *arrow of time*, i.e., since every natural process inexorably increases the entropy, one can distinguish the past from the future.

Note that the entropic change of an irreversible process is higher than a reversible one with the same exchanged heat, Q, and temperature T. More modern approaches often rewrite the inequality from Eq.(2.16) into the following equality:

$$dS_{system} = d\Phi + d\Sigma, \tag{2.18}$$

where $d\Phi \equiv \frac{\delta Q}{T}$ is recognized as the entropy change due to the external energy flow[i], known as *entropy flux*, and $d\Sigma$, or the *entropy production*, is the change due to the irreversible

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[h] In the context of thermodynamics, the word *universe* does not have a cosmological sense.

[i] If the system is open, there is also an energetic contribution due to matter flow.

processes. Along these lines, it is clear that entropy dS_{system} and $d\Phi$ might acquire positive or negative values, while entropy production is always a positive quantity,

$$d\Sigma \geq 0. \tag{2.19}$$

Interestingly, while the first law states that the energy of an isolated system is conserved, the second implies that its entropy is not and, more importantly, can only increase during natural processes. Of course, both fundamental quantities are intrinsically connected, and many applications of thermodynamics intend to characterize their changes.

2.1.1.1.4 Third law of thermodynamic

Finally, the *third law of thermodynamics* is mathematically stated as

$$T \to 0_+ \;\Rightarrow\; S \to S_0, \tag{2.20}$$

i.e., when the temperature T approaches the limiting absolute zero, the entropy approaches a constant value, S_0, independent of all macroscopic variables.

2.1.1.1.5 Brief remarks

In the context of thermodynamics, physical properties are commonly separated into two distinct categories: On the one hand, *intensive* quantities are independent of the mass or the size and number of constituents of the system; On the other, *extensive* ones are those proportional to the system's mass, number of constituents, or size. Along these lines, let us consider a thermodynamic system in equilibrium described by the macroscopic variables temperature T, volume V and pressure P. Naturally, one can also prescribe an internal energy U and entropy S. Then, suppose one can split the whole system into two equal smaller subsystems. Both partitions will maintain their previous temperature T and pressure P, while their new volume, internal energy and entropy will be divided by two ($V/2$, $U/2$ and $S/2$). Thus, it is clear that T and P are intensive quantities, while V, U and S are extensive ones. In particular, notice that extensivity also means that these properties are *additive*, i.e., the whole energy and entropy, for instance, are the sum of the subsystem's energy and entropy, respectively.

Finally, it is worth emphasizing - once again - that the laws of thermodynamics were developed and established for macroscopic systems in equilibrium. It was not necessary any considerations concerning the microscopic behaviour of matter. Surprisingly, however, it does not mean that these laws are not valid in other regimes.

2.1.2 Stochastic thermodynamics

The microscopic foundations of classical equilibrium thermodynamics were provided by the advent of statistical mechanics. It also brought a new probabilistic perspective to the understanding of natural phenomena at the molecular level. These efforts allowed the field to shift from purely phenomenological reasoning to more solid ground. Later, linear response theory contributed to the first expeditions outside the equilibrium context. More recently, however, the scenarios are even more extreme: the current high degree of control of systems and devices below the microscopic scale urged a thermodynamic description of small systems far from equilibrium. In such circumstances, essentially, one is interested in characterizing the energetics of finite objects at finite times. Biological systems at the cellular level, molecular machines, and colloidal particles trapped by optical tweezers, for instance, are paradigmatic examples of physical objects operating under these conditions. In contrast with macroscopic scenarios, the energy within small systems is of the order of $k_B T$ and its fluctuations are not negligible. In fact, deviations from the average behaviour are typical features of such regimes and carry valuable thermodynamic information.

In general, these discussions belong to the recent field of *stochastic thermodynamics* (10–15), whose developments has been successfully helping to bridge the gap between the well known macroscopic laws and the small-scale behaviour of matter. In this framework, thermodynamic systems are both driven by external classical forces and constantly influenced by the fluctuations induced by their environments. Along these lines, thermodynamic quantities, such as work, heat and entropy production, are understood as fluctuating entities specified at the phase space trajectory level and characterized by stochastic dynamical processes, often depicted by Markovian master equations. Despite the shared probabilistic spirit, stochastic thermodynamics exceeds the scope of equilibrium statistical mechanics and the linear response regime, i.e., it allows the description of general microscopic scenarios and the consideration of arbitrary non-equilibrium processes, in such a way that the connection with the well established macroscopic laws and conclusions are directly obtained once considered the statistical ensemble level. Furthermore, this perspective provided novel insights on the relationship between irreversibility and the second law of thermodynamics. Interestingly, although predicting the positivity of the *average* of entropy production, stochastic thermodynamics highlighted the existence of trajectories with negative entropy production and provided the mathematical formalism for quantifying their probabilities of occurrence.

2.1.2.1 Fluctuations theorems

Along with a more refined view of thermodynamics, the so-called ***f**luctuation **t**heorems* (FTs) represent the most influential results of the field. Initially discovered during the ’90s (16–24) and later experimentally verified in several setups (15, 25–35), the FTs were instrumental in triggering further studies on non-equilibrium systems and fostering the foundation of stochastic thermodynamics. Essentially, the FTs are general mathematical statements concerning the probability distributions of the relevant thermodynamic quantities over an ensemble of identically prepared systems. They are usually expressed according to their ***i**ntegral* (IFTs) or ***d**etailed* (DFTs) forms, given, respectively, by (12)

$$\langle e^{-\zeta}\rangle = \int d\zeta\, P(\zeta)e^{-\zeta} = 1 \tag{2.21}$$

and

$$\frac{P(\zeta)}{P(-\zeta)} = e^{-\zeta}, \tag{2.22}$$

where ζ is a functional of the stochastic trajectory, e.g., fluctuating work and heat, and $P(\zeta)$ is its respective distribution. From Eq. (2.21), one can easily use Jensen's inequality[j] and unveil the hidden inequality

$$\langle \zeta \rangle \geq 0. \tag{2.23}$$

For instance, suppose a system initially prepared in thermal equilibrium at temperature T and then decoupled with its surroundings. If the system's Hamiltonian is parametrized as $H(\lambda)$, where λ is an externally controlled parameter, work w can be performed by simply changing it from λ_i to λ_f since $w \equiv \int \frac{\partial H(\lambda)}{\partial \lambda} d\lambda$. By defining the dissipated work along with a specific work protocol $\lambda_i \to \lambda_f$ as $w_{diss} \equiv w - \Delta F_{fi}$, where $\Delta F \equiv F_f - F_i$ is the Helmholtz free energy difference for the equilibrium states associated with $H(\lambda_i)$ and $H(\lambda_f)$, one can show the following IFT

$$\langle e^{-\beta w_{diss}} \rangle = 1 \iff \langle e^{-\beta w} \rangle = e^{-\beta \Delta F} \tag{2.24}$$

and, therefore,

$$\langle w_{diss} \rangle \geq 0 \iff \langle w \rangle \geq \Delta F_{fi}, \tag{2.25}$$

where $\beta^{-1} \equiv k_B T$ with k_B the Boltzmann constant and the ensemble averages $\langle . \rangle$ are computed after performing the same protocol several - ideally infinite - times. Interestingly, these expressions make no mention of the protocol's execution speed or its specific details. In fact, it just depends on the final and initial values λ_f and λ_i. Eq. (2.24) is the emblematic - and surprising - *Jarzynski equality* (19) relating arbitrary non-equilibrium processes, $\lambda_i \to \lambda_f$, with genuine equilibrium quantities ΔF_{fi}, while the Eq. (2.25) implied by Eq. (2.24) is one of the well-known forms of the second law of thermodynamics. Notice, however, that $\langle w \rangle \geq \Delta F_{fi}$ is even more revealing than the classical thermodynamic one since it is the *average* value of work that is higher than the difference of free energy, which also means that for individual elements of the ensemble such inequality may be violated. Of course, this conclusion does not represent a contradiction with the classical result: for macroscopic systems and their energy scales, the fluctuations are not easily observed, in a way that the work performed by the execution of the same protocol are essentially equal and, consequently, their distributions are mathematically depicted by delta functions. Additionally, if $P_\Lambda(w)$ is the probability distribution of performing some work w along the trajectory defined by the protocol $\Lambda : \lambda_i \to \lambda_f$ and $P_{\tilde{\Lambda}}(w)$ is the distribution related to

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[j] For the exponential function, Jensen's inequality becomes $e^{-\langle \zeta \rangle} \geq \langle e^{-\zeta} \rangle$.

the trajectory obtained by the time-reversed protocol, $\tilde{\Lambda} : \lambda_f \to \lambda_i$, under the assumption of Markovian dynamics and initial equilibrium states for both protocols, one can show the following DFTs-like expression

$$\frac{P_\Lambda(w)}{P_{\tilde{\Lambda}}(-w)} = e^{-\beta w_{diss}} = e^{-\beta(w-\Delta F_{fi})}, \tag{2.26}$$

also known as the *Crooks theorem.* (23) Interestingly, Eq. (2.26) means the probability of observing trajectories whose work spent along with Λ is given by w is exponentially more likely than the probability of observing work $-w$ along with the reverse protocol $\tilde{\Lambda}$. In fact, their probabilities are equal iff the work performed is equal to the free energy difference, $w = \Delta F_{fi} \iff P_\Lambda(w) = P_{\tilde{\Lambda}}(-w)$. Moreover, it is easy to see that Eq. (2.26) directly implies the Jarzynski equality, Eq. (2.24)[k].

Finally, by properly identifying entropy production, Σ, along with stochastic trajectories, one can also show the following IFT for arbitrary protocols and initial conditions (12, 13)

$$\langle e^{-\frac{\Sigma}{k_B}} \rangle = 1. \tag{2.27}$$

Again, it also implies what can be seen as a more refined version of the second law of thermodynamics depicted by Eq. (2.19) concerning the average value of entropy production, such that

$$\langle \Sigma \rangle \geq 0. \tag{2.28}$$

In short, these theorems are simple equalities concerning the distributions of stochastic thermodynamic quantities. Surprisingly, they are valid even for *general* processes far from equilibrium. In this sense, despite their simplicity, they represented generalizations of the classical macroscopic thermodynamic results and provided novel insights on the underlying statistical nature of the laws of thermodynamics.

2.2 Quantum mechanics

Quantum mechanics (QM) is one of the main pillars of modern science, not only because of its remarkable accuracy and outstanding success in predicting physical phenomena but also because it represents, along with Einstein's theory of general relativity and Maxwell's of electrodynamics, our best attempt to understand the very fundamental aspects of nature. Since its early days, at the beginning of the 20th century, it became clear that the development of QM would require a novel and courageous change in the traditional way of thinking. After all, physics - as was commonly believed at the time - was not complete, and the failure of classical theories to explain the contemporary experimental observations was undeniable evidence of this defeat. Hence, despite centuries of immense accomplishment, physicists were forced to adapt in the face of empirical confrontation.

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[k] $\int dw\, P_{\tilde{\Lambda}}(-w) e^{-\beta w} = e^{-\beta \Delta F} \int dw\, P_\Lambda(w) \Rightarrow \langle e^{-\beta w} \rangle = e^{-\beta \Delta F}$.

Along these lines, the so-called ultraviolet catastrophe is a paradigmatic example of how nature's behaviour contradicted classical intuition and, in contrast, radical new hypotheses were suddenly necessary. This interesting episode is commonly seen as the birth of the quantum theory, and Max Planck (1858 - 1947) is regarded as one of its founding fathers. Latter, seminal works by Albert Einstein (1879 - 1955), Niels Bohr (1885 - 1962), Louis de Broglie (1892 - 1987), Erwin Schrödinger (1887 - 1961), Werner Heisenberg (1901 - 1976) and many others helped develop and establish the basis and mathematical structure of the theory.

During the first decades of the last century, QM flourished both from a theoretical perspective and experimental validation. The revolutionary ideas of energy quantization, particle-wave duality and the intrinsic probabilistic behaviour at the atomic scale, although highly non-intuitive, seemed to be a superior way to describe how nature works. This early progress was of fundamental importance to pave the way for the later development of quantum field theory and the conception of modern technologies, such as the groundbreaking developments of the transistor, the laser and, more recently, magnetic resonance machines. However, despite this great success, QM remained challenging conceptually. On the one hand, it was unclear how to physically interpret some fundamental aspects of the theory, such as the wave function and non-local correlations. On the other, there was a debate to understand if it was indeed a complete description of reality. Interestingly, even after one century of development and crucial progress, some of these foundational questions remain open, which, in a sense, preserve these old debates echoing throughout modern research. This, however, did not prevent the field from expanding and developing. Applications of QM to specific questions gave rise to new and exciting research fields. The birth of quantum information and computation in the '80s and their first progress during the '90s, for instance, are recent and fascinating ramifications of the quantum theory in the context of information processing.

Nowadays, QM maintains its influence as one of the most fundamental theories of modern physics and keeps changing the world consistently in several aspects ranging from the production of new materials to the development of novel - and unique - technologies. Along these lines, this section will be dedicated to briefly introducing - or reviewing - the elementary aspects of the theory and its particular mathematical formalism. Of course, it does not aim for an extensive presentation of the subject and its most modern tools. A comprehensive discussion of QM can be found in the excellent textbooks that also guided the following introduction. (36–40)

2.2.1 Mathematical description of quantum systems

Quantum theory, essentially, is mathematically written and stated with the vocabulary provided by linear algebra. In fact, the whole formalism of QM, and its basic elements, can be described by vectors and linear transformations. In this sense, complex vector spaces with inner product, known as Hilbert spaces, are the most fundamental underlying structures setting the stage for describing quantum systems, whose physical states are simply represented by vectors within these abstract entities.

Along these lines, for every quantum system, there is an associated Hilbert space $\mathcal{H}$ with the appropriate dimensionality $d := dim(\mathcal{H})$ - possibly infinity - such that its vector state is fully characterized and labelled by, according to Dirac's notation, the so-called *ket* $|\Psi\rangle \in \mathcal{H}$. From now on, let us assume only finite-dimensional Hilbert spaces. These vectors, or kets, encode all possible information concerning the physical system in question and are the quantum analogous to the usual notion of classical states in the phase space, given by $(\overrightarrow{\boldsymbol{p}}, \overrightarrow{\boldsymbol{q}})$[1]. Just like any regular vector, every ket $|\Psi\rangle$ can be represented in terms of a basis, i.e., given a set $\{|b_j\rangle, j = 1, ..., d\}$ of d linearly independent kets spanning $\mathcal{H}$, one can describe the state as the following *superposition* (linear combination)

$$|\Psi\rangle = \sum_{j=1}^{d} \alpha_j |b_j\rangle, \tag{2.29}$$

where the coefficients $\{\alpha_j, j = 1, ..., d\}$ are complex numbers. Besides, it is worth mentioning that Hilbert spaces inherit all properties and basic operations defined for arbitrary vector spaces. Along with $\mathcal{H}$, we should also define the so-called dual vector space $\mathcal{H}^*$, whose for every possible element $|\Psi\rangle$ of $\mathcal{H}$, there is a single component $\langle\Psi|$ - known as *bra* - from $\mathcal{H}^*$, such that

$$|\Psi\rangle = \sum_{j=1}^{d} \alpha_j |b_j\rangle \longleftrightarrow \langle\Psi| = \sum_{j=1}^{d} \alpha_j^* \langle b_j|, \tag{2.30}$$

where α_j^* denotes the complex conjugate of α_j. Now we have all the necessary ingredients to properly define the inner product between two elements $|\psi\rangle$ and $|\phi\rangle$ of $\mathcal{H}$ as simply as

$$\langle\psi|\phi\rangle, \tag{2.31}$$

where $\langle\psi|\phi\rangle = (\langle\phi|\psi\rangle)^*$ and $\langle\psi|\psi\rangle \geq 0$. Thus, two non-null kets are orthogonal, relative to Eq. (2.31), iff $\langle\psi|\phi\rangle = 0$. Also, it allows the identification of the norm of a ket $|\psi\rangle$ as $|||\psi\rangle|| \equiv \sqrt{\langle\psi|\psi\rangle}$. In this sense, every possible basis $\{|b_j\rangle, j = 1, ..., d\}$ of $\mathcal{H}$ should contain orthogonal and normalized (unit norm) elements, i.e., they should satisfy the orthonormality condition stated by $\langle b_j|b_k\rangle = \delta_{jk}$, where δ_{jk} is the usual Kronecker delta.

In QM, the system's state is encoded only in the "direction" of $|\psi\rangle$. In fact, any ket from the set $\{c|\Psi\rangle \in \mathcal{H} | c \in \boldsymbol{C}_{\neq 0}\}$ represents the same physical state. For this reason, and latter interpretative convenience, it is commonly assumed normalized kets for describing

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[1] Of course, the analogy only corresponds to their similar descriptive roles inside their particular theoretical frameworks.

quantum systems, $\langle\Psi|\Psi\rangle = 1$, which also implies that, given Eq. (2.29),

$$\sum_{j=1}^{d} \alpha_j^* \alpha_j = \sum_{j=1}^{d} |\alpha_j|^2 = 1. \tag{2.32}$$

Interestingly, one could add a complex phase $c = e^{i\theta}$ with unit modulus such that $|\Psi\rangle \to e^{i\theta}|\Psi\rangle$, in such a way that $\langle\Psi|\Psi\rangle = 1$ is still satisfied. Nevertheless, this phase, often called as global phase, does not affect any physical prediction obtained from $|\Psi\rangle$.

2.2.1.1 Operators and observables

In the following sections, we denote operators by $\hat{(.)}$. In this context, operators refer to linear transformations $\hat{T} : \mathcal{H} \to \mathcal{H}'$ mapping one element $|\Psi\rangle$ from a particular Hilbert space $\mathcal{H}$ to another $|\Phi\rangle$ from $\mathcal{H}'$, such that $\hat{T}|\Psi\rangle = |\Phi\rangle$ and

$$\hat{T}\left(\sum_{j=1}^{d} \alpha_j |b_j\rangle\right) = \sum_{j=1}^{d} \alpha_j (\hat{T}|b_j\rangle). \tag{2.33}$$

Nevertheless, most of the time, we are interested in operators $\hat{O}$ acting within a specific Hilbert space, such that $\hat{O} : \mathcal{H} \to \mathcal{H}$. From now on, the set of linear operators satisfying this is denominated by $\mathcal{L}(\mathcal{H})$. Without any loss of generality, let us restrain our discussion for such cases.

As shown earlier, kets can be represented in terms of any basis $\{|b_j\rangle, j = 1, ..., d\}$ of $\mathcal{H}$. Similarly, operators might be depicted by $d \times d$ matrices. In this sense, any operator $\hat{O} \in \mathcal{L}(\mathcal{H})$ is fully characterized by the complex matrix elements $o_{kj} \equiv \langle b_k|\hat{O}|b_j\rangle$ and written in terms of the outer products defined by $|b_k\rangle\langle b_j|$, such that

$$\hat{O} = \sum_{k=1}^{d} \sum_{j=1}^{d} o_{kj} |b_k\rangle\langle b_j|. \tag{2.34}$$

It is worth mentioning that any orthonormal basis of $\mathcal{H}$ is a valid and equivalent basis of description, in the sense that all possible representations are directly connected via similarity transformations. This fact gives us the freedom to perform calculations in the most suitable one. Thus, given Eqs. (2.29, 2.34), we have - in general - $\hat{O}|\Psi\rangle = \sum_{k=1}^{d}\sum_{j=1}^{d} \alpha_j o_{kj} |b_k\rangle$. In particular, the so-called identity operator $\hat{1} \in \mathcal{L}(\mathcal{H})$ that maps any ket to itself, such that $\hat{1}|\Psi\rangle = |\Psi\rangle$, is clearly obtained iff $o_{kj} = \delta_{kj}$ in the equation above. Hence,

$$\hat{1} = \sum_{j=1}^{d} |b_j\rangle\langle b_j| \tag{2.35}$$

This important equality is true for any possible basis, and it is known as the *completeness relation*. Often, we are interested in the applications of different operators in a given ket, such as $\hat{O}_2\hat{O}_1|\Psi\rangle$. Since they are depicted by matrices, the general non-commutative property is, naturally, inherited, i.e., $\hat{O}_1\hat{O}_2 \neq \hat{O}_2\hat{O}_1$. Sometimes, however, operators might commute and, for this reason, it is convenient to define the *commutator* $[,]$ between two operators as

$$[\hat{O}_1, \hat{O}_2] \equiv \hat{O}_1\hat{O}_2 - \hat{O}_2\hat{O}_1. \tag{2.36}$$

Let us present some import classes of linear operators. The Hermitian conjugate of $\hat{O}$ - or simply adjoint - defined by $\hat{O}^\dagger$, is the unique operator which guarantees that the bra $(\langle\Psi|\hat{O}^\dagger)$ is the dual vector of the ket $(\hat{O}|\Psi\rangle)$. Operationally, the matrix $\hat{O}^\dagger$ is the conjugate transpose of $\hat{O}$, which means that $\langle b_k|\hat{O}|b_j\rangle = (\langle b_j|\hat{O}^\dagger|b_k\rangle)^*$. Nevertheless, if

$$\hat{O} = \hat{O}^\dagger, \tag{2.37}$$

then $\hat{O}$ is denominated as a *Hermitian* operator. Additionally, *Unitary* operators $\hat{U}$ are those who satisfy the following equality

$$\hat{U}\hat{U}^\dagger = \hat{U}^\dagger\hat{U} = \hat{1}, \tag{2.38}$$

which also implies that they preserve the inner product, such that $\langle\psi|\phi\rangle = (\langle\psi|\hat{U}^\dagger)(\hat{U}|\phi\rangle)$. Both Hermitian and Unitary linear operators are examples of a broader class of operators, known as *Normal* ones. A Normal operators $\hat{N}$, by definition, commutes with its own Hermitian conjugate, i.e.,

$$[\hat{N}, \hat{N}^\dagger] = 0 \tag{2.39}$$

or $\hat{N}\hat{N}^\dagger = \hat{N}^\dagger\hat{N}$. Along these lines, this class of operators are accompanied by the *spectral theorem*, which states that (39): if $\hat{N} \in \mathcal{L}(\mathcal{H})$ is normal, then it is unitarily diagonalizable, i.e., there is a basis $\{|N_j\rangle, j = 1, ..., d\}$ of $\mathcal{H}$ such that

$$\hat{N} = \sum_{j=1}^{d} n_j |N_j\rangle\langle N_j|, \tag{2.40}$$

where $\{n_j, j = 1, ..., d\}$ and $\{|N_j\rangle, j = 1, ..., d\}$ are the respective eigenvalues and eigenvectors of $\hat{N}$, since $\hat{N}|N_j\rangle = n_j|N_j\rangle$. The form of Eq. (2.40) above is commonly referred to as the *spectral decomposition* of $\hat{N}$. Interestingly, if two different normal operators $\hat{N}_1$ and $\hat{N}_2$ have spectral decompositions according to the same basis, they must commute, i.e., if $\hat{N}_k = \sum_{j=1}^{d} n_{k,j}|N_j\rangle\langle N_j|$ for $k = 1, 2$ share the same eigenvectors, then it is guaranteed that $[\hat{N}_1, \hat{N}_2] = 0$.

In QM, meaningful physical quantities, such as position, momentum and spin, are known as observables and mathematically described by hermitian linear operators and the machinery presented above. Along these lines, given an observable $\hat{O} \in \mathcal{L}(\mathcal{H})$, its eigenvalues $\{o_j\}_{j=1,...,d}$ are understood as the possible outcomes of an eventual measurement performed on the quantum system. The hermiticity condition, stated by Eq. (2.37), guarantee that these values are real numbers[m].

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[m] Given Eq. (2.40), if $\hat{N} = \hat{N}^\dagger$, then $\{n_j\}_j \in \mathbb{R}$.

2.2.1.2 Projective measurements

Suppose that $\hat{B} \in \mathcal{L}(\mathcal{H})$ is the observable we are interested in measuring, with the following spectral decomposition

$$\hat{B} = \sum_{j=1}^{d} b_j |b_j\rangle\langle b_j|. \tag{2.41}$$

If $|\Psi\rangle$ is the system's state, and since $\{|b_j\rangle, j = 1, ..., d\}$ constitute a valid basis of $\mathcal{H}$, let us write it in the following representation $|\Psi\rangle = \sum_{j=1}^{d} \alpha_j |b_j\rangle$, where $\alpha_k \equiv \langle b_k|\Psi\rangle$. Notice that, in general, $|\Psi\rangle$ is in a superposition of the eigenvectors of $\hat{B}$. Once a measurement is performed, two things happen: **i)** as a result of the process, the measurement apparatus obtains one of the possible eigenvalues of $\hat{B}$; **ii)** the system's state immediately collapses into one of the superposition elements. Such state update corresponds to the eigenvector relative to the measurement outcome, i.e., if b_k is measured, then

$$|\Psi\rangle \to |\Psi'\rangle \equiv |b_k\rangle. \tag{2.42}$$

This whole event - known as a projective measurement - is seen as fundamentally probabilistic, i.e., in the orthodox presentation of QM, all information encoded by $|\Psi\rangle$ are the statistics of the outcomes, which are characterized by the coefficients $\{\alpha_j, j = 1, ..., d\}$ playing the role of probability amplitudes. In this sense, by defining the so-called projectors $\hat{\Pi}_k \equiv |b_k\rangle\langle b_k| \in \mathcal{L}(\mathcal{H})$, the probability of measuring b_k and the system collapsing to $|b_k\rangle$ is given by

$$Prob(b_k) \equiv \langle\Psi|\Pi_k|\Psi\rangle = |\alpha_k|^2 \geq 0, \tag{2.43}$$

while the collapse itself is mathematically written as

$$|\Psi'\rangle = \frac{\Pi_k|\Psi\rangle}{\sqrt{\langle\Psi|\Pi_k|\Psi\rangle}}. \tag{2.44}$$

Notice that, it means that if any posterior measurement of $\hat{B}$ is performed right after the first one, the system would still be found at the same state $|\Psi'\rangle = |b_k\rangle$ with $Prob(b_k) = 1$. Also, as expected, the normalization $\langle\Psi|\Psi\rangle = 1$ guarantees that

$$\sum_{k=1}^{d} Prob(b_k) = 1. \tag{2.45}$$

It is clear that the physical act of measuring is not being modelled at all, and the treatment above is, essentially, phenomenological. In fact, Eq. (2.43) is a fundamental *postulate* of QM and, therefore, it is not demonstrable from first principles[n].

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[n] Still today, there are several discussions on this matter, especially on foundational questions of QM. (41)

From the measurement statistics of $\hat{B}$ above, one can compute its average value simply as $\sum_{k=1}^{d} b_k Prob(b_k)$. Thus, it is easy to see that the expectation value of any given observable $\hat{O} \in \mathcal{L}(\mathcal{H})$ relative to the state $|\Psi\rangle$ can be defined as

$$\langle \hat{O} \rangle \equiv \langle \Psi | \hat{O} | \Psi \rangle. \tag{2.46}$$

It is worth mentioning that, even though $|\Psi\rangle$ might represent a single physical quantum system, in practice, such probabilities are only accessible at an ensemble level analysis, in a way that it is implicitly assumed several identical copies of the same physical ket. This identical copy setting is known as a *pure* ensemble.

2.2.1.3 Composite systems

Let us now generalize the previous formalism to include the description of - possibly - several quantum systems[o]. In many cases, the quantum system being described is composed of two or more, non necessarily equal, subsystems. If $\mathcal{H}^{(k)}$ is the Hilbert space of the kth element of a group of N subsystems, the whole Hilbert space $\mathcal{H}^{(0)}$ is constituted by the following tensor product $\mathcal{H}^{(0)} = \mathcal{H}^{(1)} \otimes \mathcal{H}^{(2)} ... \otimes \mathcal{H}^{(N)}$. Of course, each subsystem might have its own dimensionality $d^{(k)} := dim(\mathcal{H}^{(k)})$, such that $d^{(0)} = \Pi_{k=1}^{N} d^{(k)}$. The representation of possible states in $\mathcal{H}^{(0)}$ is given by the tensor product structure $|\psi^{(1)}\rangle \otimes |\psi^{(2)}\rangle ... \otimes |\psi^{(N)}\rangle = |\psi^{(1)}\psi^{(2)} ... \psi^{(N)}\rangle$, where $|\psi^{(k)}\rangle \in \mathcal{H}^{(k)}$ stands for an individual ket belonging to the kth subsystem. It means that, in the particular case in which every subsystem is prepared in the state $|\Psi^{(k)}\rangle$, the whole system is described by $|\Psi\rangle = |\Psi^{(1)}\rangle \otimes |\Psi^{(2)}\rangle ... \otimes |\Psi^{(N)}\rangle$.

For simplicity, let us focus on bipartite systems, i.e., quantum systems composed of two individual subsystems. Thus, let $\mathcal{H}^{(0)} = \mathcal{H}^{(1)} \otimes \mathcal{H}^{(2)}$ and $\{|b_j^{(1,2)}\rangle, j = 1, ..., d^{(1,2)}\}$ be a possible basis of $\mathcal{H}^{(1,2)}$. Then any bipartite state can be written as

$$|\Psi\rangle = \sum_{j=1}^{d^{(1)}} \sum_{k=1}^{d^{(2)}} a_{jk} |b_j^{(1)}\rangle \otimes |b_k^{(2)}\rangle, \tag{2.47}$$

where $a_{jk} \equiv \langle b_j^{(1)}, b_k^{(2)} | \Psi \rangle$ is the probability amplitude of finding each individual subsystem into the states $|b_j^{(1)}\rangle$ and $|b_k^{(2)}\rangle$. Eq. (2.47) above is very general. In some cases, if $a_{jk} = c_j d_k$, then the whole system can be written as

$$|\Psi\rangle = |\phi^{(1)}\rangle \otimes |\phi^{(2)}\rangle, \tag{2.48}$$

where $|\phi^{(1)}\rangle = \sum_{j=1}^{d^{(1)}} c_j |b_j^{(1)}\rangle$ and $|\phi^{(2)}\rangle = \sum_{k=1}^{d^{(2)}} d_k |b_k^{(2)}\rangle$, i.e., for each subsystem, one can attribute an individual local state $|\phi^{(1,2)}\rangle$ that it is independent of the other. Whenever the previous form of Eq. (2.48) is obtained, the whole system is denominated *separable*,

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[o] Notice that the majority of the machinery presented here also works for a single quantum systems that has several degrees of freedom, such as orbital motion, spin, etc.

and we have a product state. Otherwise, the subsystems are non-separable and, therefore, called *entangled*. Entanglement is a genuine quantum property that, essentially, means the different quantum systems have fundamentally correlated states, regardless of their physical spatial distance. Interestingly, it implies that the whole entangled system is not understood as the simple composition of individual subsystems but an indivisible entity instead.

In this context, local operators $\hat{O}^{(k)} \in \mathcal{L}(\mathcal{H}^{(k)})$ are the ones that act on individual subsystems and, therefore, specific Hilbert spaces. In a global perspective, however, a local operator acting in the subsystem (2) of $|\psi^{(1)}\rangle \otimes |\psi^{(2)}\rangle$, for instance, translates to

$$\left(\hat{1}^{(1)} \otimes \hat{O}^{(2)}\right) |\psi^{(1)}\rangle \otimes |\psi^{(2)}\rangle = |\psi^{(1)}\rangle \otimes \hat{O}^{(2)}|\psi^{(2)}\rangle, \tag{2.49}$$

which means that $\hat{O}^{(2)}$ acts on $|\psi^{(2)}\rangle$, while $|\psi^{(1)}\rangle$ remains unchanged due to the identity operator $\hat{1}^{(1)}$. Besides, one could also be interested in applying the operators $\hat{O}^{(1)}$ and $\hat{O}^{(2)}$ simultaneously. In this case, the whole operator is written as $\hat{O}^{(1)} \otimes \hat{O}^{(2)}$ and

$$\left(\hat{O}^{(1)} \otimes \hat{O}^{(2)}\right) |\psi^{(1)}\rangle \otimes |\psi^{(2)}\rangle = \hat{O}^{(1)}|\psi^{(1)}\rangle \otimes \hat{O}^{(2)}|\psi^{(2)}\rangle. \tag{2.50}$$

Along these lines, bipartite states can be cast in a very convenient and special form, given by the Schmidt decomposition. Since this procedure is the basis of this work, let us discuss it in more detail.

2.2.1.3.1 The Schmidt decomposition

The Schmidt decomposition is a very useful theorem concerning the representation form of pure bipartite quantum states (or any composite one with a bipartite separation, actually). Its convenience has far-reaching consequences and applications in quantum theory, especially in the context of quantum information and quantum computation. Essentially, it claims that any pure bipartite state can be written compactly as a single sum of correlated orthonormal basis. In fact, as briefly sketched below, this is a direct consequence of a more general result concerning matrix factorization, known as **S**ingular **V**alue **D**ecomposition (SVD for short). Despite its simplicity and aesthetical appeal, the Schmidt decomposition facilitates both the entanglement analysis and the computation of reduced states[p] when dealing with such systems. It is also worth mentioning that this tool is closely related to the concept of state purification.

Consider a pure bipartite quantum state $|\Psi\rangle \in \mathcal{H}^{(0)} = \mathcal{H}^{(1)} \otimes \mathcal{H}^{(2)}$, such that $dim(\mathcal{H}^{(1,2)}) = d^{(1,2)}$ and, without any loss of generality, $d^{(1)} \leq d^{(2)}$. Given a pair of local orthonormal basis $\{|b_j^{(1,2)}\rangle, j = 1, ..., d^{(1,2)}\}$ for $\mathcal{H}^{(1,2)}$, we know that $|\Psi\rangle$ can be written according to Eq. (2.47). Notice that this general expression contains a double

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[p] Formally presented in Section (2.2.1.4.2).

sum $\sum_{j=1}^{d^{(1)}}\sum_{k=1}^{d^{(2)}}$, each one relative to its respective subsystem's Hilbert space. Clearly, this represents a superposition over all possible combination of basis elements, where $|a_{jk}|^2$ quantify the probability associated with the ket $|b_j^{(1)}\rangle \otimes |b_k^{(2)}\rangle$. Alternatively, the coefficients a_{jk} can be seen as the entries of a $d^{(1)} \times d^{(2)}$ matrix $\overleftrightarrow{A}$, such that $a_{jk} = [\overleftrightarrow{A}]_{jk}$. The SVD guarantee the following matrix factorization below

$$\overleftrightarrow{A} = \overleftrightarrow{L}\,\overleftrightarrow{\Lambda}\,\overleftrightarrow{R}^{\dagger}, \tag{2.51}$$

where $\overleftrightarrow{L}$ and $\overleftrightarrow{R}$ are matrices with orthogonal columns, i.e., $\overleftrightarrow{L}^{\dagger}\overleftrightarrow{L} = \overleftrightarrow{R}^{\dagger}\overleftrightarrow{R} = \overleftrightarrow{1}$, and $\overleftrightarrow{\Lambda}$ is a diagonal positive semi-definite matrix. Since we are assuming $d^{(1)} \leq d^{(2)}$, both $\overleftrightarrow{L}$ and $\overleftrightarrow{\Lambda}$ are square $d^{(1)} \times d^{(1)}$ matrices, while $\overleftrightarrow{R}$ is a $d^{(2)} \times d^{(1)}$ one[q]. The diagonal elements $\{\lambda_j, j = 1, ..., d^{(1)}\}$ of $\overleftrightarrow{\Lambda}$ are called its singular values, and the number $n \leq d^{(1)}$ of non-zero λ_j is known as the Schmidt rank. Thus,

$$a_{jk} = \sum_{\eta=1}^{n} L_{j\eta}\lambda_{\eta}R^{*}_{k\eta}, \tag{2.52}$$

and, therefore,

$$|\Psi\rangle = \sum_{\eta=1}^{n} \lambda_{\eta}|\varphi_{\eta}^{(1)}\rangle \otimes |\varphi_{\eta}^{(2)}\rangle, \tag{2.53}$$

where $|\varphi_{\eta}^{(1)}\rangle \equiv \sum_{j=1}^{d^{(1)}} L_{j\eta}|b_j^{(1)}\rangle$ and $|\varphi_{\eta}^{(2)}\rangle \equiv \sum_{k=1}^{d^{(2)}} R^{*}_{k\eta}|b_k^{(2)}\rangle$. Additionally, the normality condition of $|\Psi\rangle$ and the $\overleftrightarrow{L}$ ($\overleftrightarrow{R}$) column's orthogonality guarantee that $\sum_{j=1}^{n}\lambda_j^2 = 1$ and $\langle\varphi_m^{(1,2)}|\varphi_n^{(1,2)}\rangle = \delta_{mn}$, respectively. Eq. (2.53) is the well known Schmidt decomposition of $|\Psi\rangle$ in its full glory, where the local kets $\{|\varphi_j^{(1)}\rangle, j = 1, ..., d^{(1)}\}$ and $\{|\varphi_j^{(2)}\rangle, j = 1, ..., d^{(2)}\}$ form an orthonormal basis for $\mathcal{H}^{(1)}$ and $\mathcal{H}^{(2)}$, called Schmidt basis, and the singular values λ_j are also known as the Schmidt coefficients of $|\Psi\rangle$[r]. These coefficients are unambiguously defined, while the Schmidt basis are unique up to eventual degenerate coefficients and phases. Such form is general and far from being intuitive, and, despite the obvious simplification compared with Eq. (2.47), it has many interesting features that justify its use: notice that the double sum is changed for a single one bounded by the Schmidt rank $n \leq d^{(1)}$, which means that regardless the dimension $d^{(2)}$ only an n-dimensional subspace of $\mathcal{H}^{(2)}$ is relevant for the whole state description; besides, it becomes evident that in order to have entangled bipartite systems, or non-separable $|\Psi\rangle \neq |\varphi^{(1)}\rangle \otimes |\varphi^{(2)}\rangle$, it is required at least two non-zero Schmidt coefficients, i.e., $|\Psi\rangle$ is an entangled state iff $n >1$; plus, it gives all necessary information for writing the reduced states (as discussed in Section (2.2.1.4.2)).

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[q] If $d^{(1)} \geq d^{(2)}$, their forms would be altered: $\overleftrightarrow{R}$ would be a square matrix while $\overleftrightarrow{L}$ would be rectangular.

[r] Depending on the reference, sometimes the square of the singular values are denominated as the Schmidt coefficients.

2.2.1.4 Density operator

The framework presented until now was built to describe pure states $|\Psi\rangle \in \mathcal{H}$. As mentioned earlier, every physical ket encodes the probabilities associated with measurements performed on a chosen basis. Such statistics, however, is only observed at the ensemble level, i.e., after the access of a collection of identical copies of $|\Psi\rangle$. Although feasible, it is clear that this is a particular case of a more general ensemble. In most realistic scenarios, one has access to a statistical mixture of N arbitrary states $\{P_\eta, |\Psi_\eta\rangle \in \mathcal{H}, \eta = 1, ..., N\}$, where $\{P_\eta\} \geq 0$ with $\sum_{\eta=1}^{N} P_\eta = 1$ characterizes the distribution of pure states $|\Psi_\eta\rangle$. The mathematical entity representing quantum ensembles is known as density operators or density matrices and written as

$$\hat{\rho} \equiv \sum_{\eta=1}^{N} P_\eta |\Psi_\eta\rangle\langle\Psi_\eta| \in \mathcal{L}(\mathcal{H}). \tag{2.54}$$

If $P_j = 1$ and $P_\eta = 0$ for all $\eta \neq j$, then the quantum state $\hat{\rho} = |\Psi_j\rangle\langle\Psi_j|$ is called pure. Otherwise, it is referred to as a mixed state. Eq. (2.54) is the most general representation of a quantum system. In fact, the whole formalism of QM can be stated in terms of density operators $\hat{\rho}$. Notice that, instead of being represented by kets, states are depicted by operators according to this framework. Also, in contrast with the probabilities mentioned in the context of pure ensembles, the distribution of states $\{P_\eta\}$ is fully classical, in the sense that it only captures our ignorance concerning the preparation - or access - of possible quantum states. It is worth mentioning the pure states within the set $\{|\Psi_\eta\rangle\}$ are not necessarily orthogonal. Nevertheless, since $\hat{\rho}$ is clearly hermitian, one can write it conforming to its spectral decomposition, such that

$$\hat{\rho} = \sum_{j=1}^{d} p_j |\varphi_j\rangle\langle\varphi_j|, \tag{2.55}$$

where $\{|\varphi_j\rangle, j = 1, ..., d\}$ is a basis of $\mathcal{H}$ and $\{p_j\} \geq 0$ with $\sum_j^d p_j = 1$. Along these lines, it is clear that density matrices correspond to a particular class of operators within $\mathcal{L}(\mathcal{H})$, satisfying some properties to characterize physical systems. The corresponding density matrices' subset will be represented by $\mathscr{D}(\mathcal{H})$. Mathematically, any $\hat{\rho} \in \mathscr{D}(\mathcal{H})$ should meet the following conditions:

1. **Hermitian:** $\hat{\rho} = \hat{\rho}^\dagger$;
2. **Unit trace:** $tr\{\hat{\rho}\} = 1$[s];
3. **Positive semi-definite:** $\hat{\rho} \geq 0$ or $\{p_j\} \geq 0$.

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[s] The trace $tr\{\hat{O}\}$ of any operator $\hat{O}$ is simply the sum of its diagonal elements. Since this quantity is independent of the representation choice, one can use any basis to compute it.

While condition **1.** implies real eigenvalues, condition **2.** states the normalization of $\hat{\rho}$ or $\sum_{j=1}^{d} p_j = 1$ and condition **3.** guarantee positive probabilities, $p_j \geq 0$ for all j. Besides, every density matrix $\hat{\rho}$ satisfies the following inequality

$$tr\{\hat{\rho}^2\} \leq 1. \tag{2.56}$$

Interestingly, by computing Eq. (2.56), one can easily verify if the state $\hat{\rho}$ is pure or mixed. Notice that $tr\{\hat{\rho}^2\} = 1$ iff $\hat{\rho} = |\Psi\rangle\langle\Psi|$ is pure. Otherwise, it is mixed. For this reason, Eq. (2.56) is commonly known as state purity.

2.2.1.4.1 Projective measurements

Concerning measurements and observables. Let us suppose, again, the observable $\hat{B} = \sum_{j=1}^{d} b_j |b_j\rangle\langle b_j|$. If a projective measurement is performed in an ensemble characterized by Eq. (2.55), the probability of obtaining b_k is

$$Prob(b_k) \equiv tr\{\hat{\Pi}_k \hat{\rho}\} = \sum_{j=1}^{d} p_j |\langle b_k|\varphi_j\rangle|^2 \geq 0, \tag{2.57}$$

which is, essentially, a sum over the probability of observing b_k conditioned by each possible element of the mixture $\{p_j, |\varphi_j\rangle, j = 1, ..., d\}$. After the measurement, as expected, the new state is pure and given by

$$\hat{\rho}' \equiv \frac{\hat{\Pi}_k \hat{\rho} \hat{\Pi}_k^\dagger}{tr\{\hat{\Pi}_k \hat{\rho}\}} = |b_k\rangle\langle b_k|. \tag{2.58}$$

From the expressions above, the average value of these measurements, $\langle\hat{B}\rangle$, can be easily computed by $\sum_{k=1}^{d} b_k Prob(b_k)$. It is straightforward to check that $\langle\hat{B}\rangle = tr\{\hat{B}\hat{\rho}\}$. This previous relation can be generalized to any observable $\hat{O} \in \mathcal{L}(\mathcal{H})$, such that its expectation value $\langle\hat{O}\rangle$ relative to the ensemble $\hat{\rho}$ is defined as[t]

$$\langle\hat{O}\rangle \equiv tr\{\hat{O}\hat{\rho}\} = tr\{\hat{\rho}\hat{O}\}. \tag{2.59}$$

2.2.1.4.2 Reduced states

If the quantum system of interest is composed of different subsystems, the density operator formalism provide a straightforward manner to describe them. Often, one has access only to a part of a much broader quantum system, in a way that it is impossible to obtain the whole state description. In this sense, the reduced density operators are the representative ones for describing local states.

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[t] Due to the cyclic property of the trace, the equality $tr\{\hat{A}\hat{B}\} = tr\{\hat{B}\hat{A}\}$ is satisfied for any pair of operators $\hat{A}$ and $\hat{B}$.

Let us suppose a bipartite system, represented by $\hat{\rho}^{(0)} \in \mathscr{D}(\mathcal{H}^{(0)})$ and $\mathcal{H}^{(0)} = \mathcal{H}^{(1)} \otimes \mathcal{H}^{(2)}$. The reduced density operators are defined by

$$\hat{\rho}^{(1)} \equiv tr_2\{\hat{\rho}^{(0)}\} \in \mathscr{D}(\mathcal{H}^{(1)}), \tag{2.60}$$

$$\hat{\rho}^{(2)} \equiv tr_1\{\hat{\rho}^{(0)}\} \in \mathscr{D}(\mathcal{H}^{(2)}), \tag{2.61}$$

where $tr_k\{(.)\}$ is the partial trace over subspace k. Of course, these quantities are genuine density operators and, therefore, inherit all desired properties. In this sense, the statistics of local observables agrees with the expected behaviour, i.e., suppose one perform measurements of an observable $\hat{O}^{(1)}$ in the subsystem (1), then

$$\langle \hat{O}^{(1)} \rangle \equiv tr\left\{\left(\hat{O}^{(1)} \otimes \hat{1}^{(2)}\right)\hat{\rho}^{(0)}\right\} = tr_1\left\{\hat{O}^{(1)}\hat{\rho}^{(1)}\right\}. \tag{2.62}$$

If the whole system is described by $\hat{\rho}^{(0)} = \hat{\rho}^{(1)} \otimes \hat{\rho}^{(2)}$, the state is separable, such that the reduced density matrices are clearly $\hat{\rho}^{(1,2)} = tr_{2,1}\{\hat{\rho}^{(0)}\}$. In these cases, access to the local descriptions is enough to characterize the whole system. Nevertheless, if $\hat{\rho}^{(0)} \neq \hat{\rho}^{(1)} \otimes \hat{\rho}^{(2)}$, then the subsystems are somehow correlated, in a way that even knowing both individual local states, $\hat{\rho}^{(1,2)}$, one still cannot infer the whole state $\hat{\rho}^{(0)}$.

Let us now consider the particular case in which the whole bipartite system is described by a pure state, such that $\hat{\rho}^{(0)} = |\Psi\rangle\langle\Psi|$ and, without any loss of generality, $d^{(1)} \leq d^{(2)}$. Thus, there is no classical uncertainty concerning the ensemble. Interestingly, as will be shown below, this is not necessarily true for the subsystems. As we saw, in general, any ket $|\Psi\rangle$ can be written as Eq. (2.47). However, the Schmidt decomposition presented in Eq. (2.53) provides a more convenient form. Along these lines, the whole state can be cast in the following form

$$\hat{\rho}^{(0)} = \sum_{\eta,\alpha=1}^{n} \lambda_\eta \lambda_\alpha |\varphi_\eta^{(1)}\rangle\langle\varphi_\alpha^{(1)}| \otimes |\varphi_\eta^{(2)}\rangle\langle\varphi_\alpha^{(2)}|, \tag{2.63}$$

such that the local states can be immediately computed,

$$\hat{\rho}^{(1)} = \sum_{\eta=1}^{n} \lambda_\eta^2 |\varphi_\eta^{(1)}\rangle\langle\varphi_\eta^{(1)}|, \tag{2.64}$$

$$\hat{\rho}^{(2)} = \sum_{\eta=1}^{n} \lambda_\eta^2 |\varphi_\eta^{(2)}\rangle\langle\varphi_\eta^{(2)}|. \tag{2.65}$$

Hence, as long the whole system is pure, its Schmidt decomposition gives all necessary information for inferring the local spectral decompositions above, i.e., the square of the Schmidt coefficients, $\{\lambda_\eta^2(t), \eta = 1, ..., n\}$, characterize the distributions across the pure states given by the Schmidt basis, $\{|\varphi_\eta^{(1,2)}(t)\rangle, \eta = 1, ..., n\}$. Notice that, despite having no uncertainty from a global perspective, the local subsystems are represented by mixed states with identical probabilities. In particular, since by hypotheses, $d^{(2)} \geq d^{(1)}$ the subsystem (2) must necessarily contain $(d^{(2)} - n)$ null eigenvalues. Interestingly, this is true for any conceivable bipartite system, regardless of the dimensions in question. Such a non-intuitive result is a direct consequence of entanglement: as mentioned earlier in Section (2.2.1.3.1), for $|\Psi\rangle$ to be entangled it is required at least two non-zero Schmidt coefficients, i.e., the Schmidt rank $n > 1$. In contrast, if $n = 1$ such that $\lambda_\eta = \delta_{k\eta}$, then $\hat{\rho}^{(1,2)} = |\varphi_k^{(1,2)}\rangle\langle\varphi_k^{(1,2)}|$, and the whole system is clearly separable,

$$|\Psi\rangle = |\varphi_k^{(1)}\rangle \otimes |\varphi_k^{(2)}\rangle \rightarrow \hat{\rho}^{(0)} = |\varphi_k^{(1)}\rangle\langle\varphi_k^{(1)}| \otimes |\varphi_k^{(2)}\rangle\langle\varphi_k^{(2)}|. \tag{2.66}$$

It is worth mentioning that the reasoning above is also commonly explored the other way around. Given a quantum system (1) described by $\hat{\rho}^{(1)} \in \mathscr{D}(\mathcal{H}^{(1)})$, by adding an auxiliary system (2), the former can be seen as a subsystem of a bigger pure one depicted by $|\Psi\rangle$, i.e., $\hat{\rho}^{(1)} = tr_2\{|\Psi\rangle\langle\Psi|\}$. This procedure is known as purification of $\hat{\rho}^{(1)}$.

2.2.2 Quantum dynamics

In the previous subsection, we presented the mathematical tools and formalism for describing quantum systems. Let us now briefly discuss how to express their time evolution considering the different possible contexts.

2.2.2.1 Isolated and closed system dynamics

The most simple dynamical scenario consists of *isolated* and *closed* quantum systems. By definition, isolated systems do not interact - in any way - with any other kind of object, classical or quantum. In these cases, the described system is fully quantized, and no other external entity is included - implicitly or explicitly - in the picture, i.e., the system in question represents the totality of elements in the context under scrutiny. Consequently, an isolated quantum system evolves *autonomously* in time, uninfluenced by anything else outside its own existence. Of course, the whole system itself may be constituted by individual interacting parts. In contrast, closed quantum systems represent less restrictive scenarios. It is allowed the presence of external interaction with classical agents, which is often justified by semi-classical reasoning. In these cases, the considered influences are implicit, and the totality of elements is not fully quantized. In general, such situations portray quantum systems evolving in time according to externally controlled (deterministic) fields driving its dynamics.

Mathematically, both cases are differentiated by the eventual time-dependency of their time-translation generator. On the one hand, isolated systems have fixed Hamiltonians. On the other hand, the external interaction considered in closed systems induces time-dependent ones. Interestingly, despite the fundamental - and subtle - differences, their dynamic behaviour is described by the same functional form.

Thus, let us proceed considering a closed quantum system at time t represented by $|\Psi(t)\rangle \in \mathcal{H}$. In general, given the initial state $|\Psi(t_0)\rangle$, we are interested in describing

$|\Psi(t)\rangle$ at any subsequent time $t \geq t_0$. Formally, this task is performed by the so-called time-evolution operator $\hat{\mathcal{U}}(t,t_0) \in \mathcal{L}(\mathcal{H})$, such that

$$|\Psi(t)\rangle = \hat{\mathcal{U}}(t,t_0)|\Psi(t_0)\rangle. \tag{2.67}$$

Essentially, $\hat{\mathcal{U}}(t,t_0)$ is the linear operator that maps any initial physical ket to a time-evolved one. Under the general requirements of $\underset{t\to t_0}{lim}\hat{\mathcal{U}}(t,t_0) = \hat{1}$, the state normalization $\langle\Psi(t)|\Psi(t)\rangle = 1$ for all t and map composition $\hat{\mathcal{U}}(t_2,t_0) = \hat{\mathcal{U}}(t_2,t_1)\hat{\mathcal{U}}(t_1,t_0)$, one can show that $\hat{\mathcal{U}}(t,t_0)$ must be unitary, $\hat{\mathcal{U}}(t,t_0)\hat{\mathcal{U}}^\dagger(t,t_0) = \hat{1}$, and satisfies the following differential equation

$$i\hbar\frac{d}{dt}\hat{\mathcal{U}}(t,t_0) = \hat{H}(t)\hat{\mathcal{U}}(t,t_0), \tag{2.68}$$

where $\hbar$ is the Planck's constant, and $\hat{H}(t) = \hat{H}^\dagger(t) \in \mathcal{L}(\mathcal{H})$ is the - possibly - time-dependent Hamiltonian and the time-translation generator of this dynamics. The general solution of Eq. (2.68) above is given by

$$\hat{\mathcal{U}}(t,t_0) = \overleftarrow{\mathcal{T}}e^{-\frac{i}{\hbar}\int_{t_0}^{t}ds\,\hat{H}(s)} \tag{2.69}$$

where $\overleftarrow{\mathcal{T}}$ is the chronological time-ordering operator. Of course, as mentioned earlier, if the system is isolated then $\hat{H}$ is constant, and the time-evolution operator is considerably simpler:

$$\hat{\mathcal{U}}(t,t_0) = e^{-\frac{i}{\hbar}\hat{H}(t-t_0)}. \tag{2.70}$$

Finally, combining Eqs. (2.67, 2.68) one obtains the usual *Schrödinger equation* for describing the state's dynamics,

$$i\hbar\frac{d}{dt}|\Psi(t)\rangle = \hat{H}(t)|\Psi(t)\rangle. \tag{2.71}$$

Alternatively, if the system of interest is initially described by a mixed state $\hat{\rho}(t_0) = \sum_{j=1}^{d} p_j|\varphi_j(t_0)\rangle\langle\varphi_j(t_0)| \in \mathscr{D}(\mathcal{H})$, each element of the ensemble will certainly time evolve according to Eq. (2.71) above, such that $|\varphi_j(t)\rangle = \hat{\mathcal{U}}(t,t_0)|\varphi_j(t_0)\rangle$. Thus, at any later time $t \geq t_0$, the density matrix is given by

$$\hat{\rho}(t) \equiv \hat{\Phi}_{t,t_0}\hat{\rho}(t_0) = \hat{\mathcal{U}}(t,t_0)\hat{\rho}(t_0)\hat{\mathcal{U}}^\dagger(t,t_0), \tag{2.72}$$

where

$$\hat{\Phi}_{t,t_0} : \mathscr{D}(\mathcal{H}) \to \mathscr{D}(\mathcal{H}) \tag{2.73}$$

is the so-called (linear) dynamical map representing the unitary time evolution[u]. Along these lines, it is straightforward to obtain the density matrix counterpart of Eq. (2.71) for the equation of motion, given by the so-called *Liouville-von Neumann equation*,

$$i\hbar\frac{d}{dt}\hat{\rho}(t) = [\hat{H}(t),\hat{\rho}(t)]. \tag{2.74}$$

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[u] Notice that $\hat{\Phi}_{t,t_0}$ acts on an operator instead of a ket. For this reason, these linear operators are commonly known as *superoperators*.

It is important to highlight that the eigenvalues $\{p_j, j = 1, ..., d\}$ of $\hat{\rho}(t)$ remain invariant for this class of time evolution.

In short, the whole dynamics of both isolated and closed systems are fully characterized once having access to initial conditions and the unitaries $\hat{\mathcal{U}}(t, t_0)$, written as functionals of the Hamiltonians, mapping states at different instants of time.

2.2.2.2 Open systems dynamics

This class of dynamics is fundamentally distinct from the isolated and closed ones. As the name suggests, open quantum systems consist of physical systems that explicitly interact with other - possibly many - quantum objects. Differently from the other cases, as a consequence of the interaction, the dynamics of open systems are unavoidably coupled and correlated to their environments, which directly affect their time evolutions and lead to the phenomena of decoherence and dissipation. More specifically, their equation of motion is no longer unitary nor described by Eq. (2.74) in such a way that a more general description formalism is required. Along these lines, an individual subsystem of a larger entity is - in general - treated as an open quantum system. As discussed earlier in Section (2.2.1.4.2), subsystems are characterized by reduced states. Therefore, essentially, we are interested in finding their dynamical equations. Solving this task is the most fundamental objective of the subfield known as open quantum systems and is of imperative importance for understanding the complex behaviour of quantum matter and the development of future quantum devices. It is worth mentioning that open systems represent the standard approach for many realistic scenarios: the intrinsic fragility of quantum systems means that they are easily disturbed by external influences. Nevertheless, if the interactions are sufficiently weak, the system might be treated as approximately isolated. Let us focus on the general aspects of open system dynamics.

Suppose the system of interest is described, at any time t, by $\hat{\rho}^{(1)}(t) \in \mathscr{D}(\mathcal{H}^{(1)})$ and corresponds to a subsystem of a larger isolated quantum system depicted by $\hat{\rho}^{(0)} \in \mathscr{D}(\mathcal{H}^{(0)})$, such that $\mathcal{H}^{(0)} = \mathcal{H}^{(1)} \otimes \mathcal{H}^{(2)}$, where $\mathcal{H}^{(2)}$ is the Hilbert space that encompasses the environment of (1). Notice this configuration establishes a bipartition between the described system and "everything else". Since the total system is isolated - by hypotheses - given an initial state $\hat{\rho}^{(0)}(t_0)$, its time evolution is guaranteed to be unitary, such that

$$\hat{\rho}^{(0)}(t) = \hat{\mathcal{U}}^{(0)}(t, t_0)\hat{\rho}^{(0)}(t_0)\hat{\mathcal{U}}^{(0)\dagger}(t, t_0), \tag{2.75}$$

where $\hat{\mathcal{U}}^{(0)}(t, t_0) = e^{-\frac{i}{\hbar}\hat{H}^{(0)}(t-t_0)} \in \mathcal{L}(\mathcal{H}^{(0)})$ is its time evolution operator, and $\hat{H}^{(0)} \in \mathcal{L}(\mathcal{H}^{(0)})$ is the Hamiltonian relative to the whole bipartition. This Hamiltonian have the following structure

$$\hat{H}^{(0)} := \hat{H}^{(1)} \otimes \hat{1}^{(2)} + \hat{1}^{(1)} \otimes \hat{H}^{(2)} + \hat{H}_{int}, \tag{2.76}$$

where $\hat{H}^{(1,2)} \in \mathcal{L}(\mathcal{H}^{(1,2)})$ are the bare Hamiltonians for each subsystem, and $\hat{H}_{int} \in \mathcal{L}(\mathcal{H}^{(0)})$ is the term representing all the physical interactions between (1) and (2). It is important to highlight the fact the bare Hamiltonians are local operators restricted to their individual subspaces while the interaction is clearly non-local, in the sense that it acts on the total Hilbert space.

According to Section (2.2.1.4.2), at any time t, the local states are simply

$$\hat{\rho}^{(1,2)}(t) = tr_{2,1}\{\hat{\mathcal{U}}^{(0)}(t,t_0)\hat{\rho}^{(0)}(t_0)\hat{\mathcal{U}}^{(0)\dagger}(t,t_0)\}. \tag{2.77}$$

Thus, using Eqs. (2.74, 2.76, 2.77), it is straightforward to show that their exact dynamical equations are

$$i\hbar\frac{d}{dt}\hat{\rho}^{(1,2)}(t) = tr_{2,1}\{[\hat{H}^{(0)},\hat{\rho}^{(0)}]\} = [\hat{H}^{(1,2)},\hat{\rho}^{(1,2)}(t)] + tr_{2,1}\{[\hat{H}_{int},\hat{\rho}^{(0)}]\}, \tag{2.78}$$

where the commutator $[\hat{H}^{(1,2)},\hat{\rho}^{(1,2)}(t)]$ resembles the contribution that appears in Eq. (2.74) and $tr_{2,1}\{[\hat{H}_{int},\hat{\rho}^{(0)}]\}$ is an extra component due to the interaction term, $\hat{H}_{int}$. While the former is the unitary part of the dynamics, the latter contains non-unitary contributions[v]. It is clear that the role played by the interaction is of extreme relevance to the local dynamics. In fact, one can easily check that its absence would imply that both subsystems would be individually isolated and, therefore, evolving in time independently, i.e., $\hat{H}^{(0)} = \hat{H}^{(1)}\otimes\hat{1}^{(2)} + \hat{1}^{(1)}\otimes\hat{H}^{(2)}$ and $i\hbar\frac{d}{dt}\hat{\rho}^{(1,2)}(t) = [\hat{H}^{(1,2)},\hat{\rho}^{(1,2)}(t)]$. Also, from a global perspective, the interaction is responsible for inducing the formation of both classical and quantum correlations within the system in a way that $\hat{\rho}^{(0)}(t) \neq \hat{\rho}^{(1)}(t)\otimes\hat{\rho}^{(2)}(t)$ for general situations. Of course, the resulting local dynamics of subsystem (1) fundamentally depends on the nature of (2) that, in principle, could be as simple as a single qubit or a complex many-body system. Nevertheless, in many scenarios involving open quantum systems, it is commonly assumed that (2) is a reservoir with an infinite number of degrees of freedom or a large heat bath. These situations, as expected, might be very complicated to be analysed by the exact expressions above or even treated numerically. For this reason, the usual approaches and techniques rely on approximative methods and different hypotheses aiming to simplify the description, which also restrains the analysis for specific regimes of validity. Along these lines, initial uncorrelated states, weak-coupling and Markovian dynamics represent the most common assumptions leading to the orthodox microscopic derivations of the phenomenological master equations.

As we can see, the interaction breaks the unitary mapping given by Eq. (2.72). This relationship, however, might be generalized by defining the dynamical map $\hat{\Lambda}^{(1)}_{t,t_0} : \mathscr{D}(\mathcal{H}^{(1)}) \to \mathscr{D}(\mathcal{H}^{(1)})$, such that

$$\hat{\rho}^{(1)}(t) \equiv \hat{\Lambda}^{(1)}_{t,t_0}\hat{\rho}^{(1)}(t_0) = tr_2\{\hat{\mathcal{U}}^{(0)}(t,t_0)\hat{\rho}^{(0)}(t_0)\hat{\mathcal{U}}^{(0)\dagger}(t,t_0)\}. \tag{2.79}$$

Any physical dynamical map of this kind should be completely positive and trace-preserving, also known as a CPTP-map, i.e.,

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[v] This operator might contain terms of the following form $[(.),\hat{\rho}^{(1,2)}(t)]$ as well. The remaining part, however, is non-unitary.

1. **Completely positive:** $\hat{\Lambda}^{(1)}_{t,t_0}\hat{\rho}^{(1)}(t_0) \geq 0$;
2. **Trace-preserving:** $tr\{\hat{\Lambda}^{(1)}_{t,t_0}\hat{\rho}^{(1)}(t_0)\} = tr\{\hat{\rho}^{(1)}(t_0)\} = 1$.

Similarly to the time evolution operator when considering physical kets, these conditions are the most basic requirements that guarantee a linear mapping between proper density matrices. Thus, the whole dynamics is fully characterized by a set of CPTP dynamical maps, $\{\hat{\Lambda}^{(1)}_{t,t_0}, t \geq t_0\}$, describing the density matrix throughout the time evolution. In some scenarios, the set of dynamical maps satisfies the so-called semigroup property $\hat{\Lambda}^{(1)}_{t_2,t_0} = \hat{\Lambda}^{(1)}_{t_2,t_1}\hat{\Lambda}^{(1)}_{t_1,t_0}$ for $t_2 \geq t_1 \geq t_0$ which also implies the usual Lindblad-like form for master equations.

For instance, let us consider initially uncorrelated systems, such that the whole bipartite system is depicted by a product state $\hat{\rho}^{(0)}(t_0) = \hat{\rho}^{(1)}(t_0) \otimes \hat{\rho}^{(2)}(t_0)$. If the spectral decomposition of subsystem (2) at time t_0 is given by

$$\hat{\rho}^{(2)}(t_0) = \sum_{\alpha=1}^{d^{(2)}} p_\alpha(t_0)|\varphi^{(2)}_\alpha(t_0)\rangle\langle\varphi^{(2)}_\alpha(t_0)|, \tag{2.80}$$

then Eq. (2.79) becomes

$$\hat{\rho}^{(1)}(t) = \hat{\Lambda}^{(1)}_{t,t_0}\hat{\rho}^{(1)}(t_0) = \sum_{\alpha=1}^{d^{(2)}}\sum_{\beta=1}^{d^{(2)}} \hat{K}^{(1)}_{\beta\alpha}(t,t_0)\hat{\rho}^{(1)}(t_0)\hat{K}^{(1)\dagger}_{\beta\alpha}(t,t_0), \tag{2.81}$$

where

$$\hat{K}^{(1)}_{\beta\alpha}(t,t_0) \equiv \sqrt{p_\alpha(t_0)}\langle\varphi^{(2)}_\beta(t_0)|\hat{\mathcal{U}}^{(0)}(t,t_0)|\varphi^{(2)}_\alpha(t_0)\rangle \in \mathcal{L}(\mathcal{H}^{(1)}) \tag{2.82}$$

and $\sum_{\alpha,\beta=1}^{d^{(2)}} \hat{K}^{(1)\dagger}_{\beta\alpha}(t,t_0)\hat{K}^{(1)}_{\beta\alpha}(t,t_0) = \hat{1}^{(1)}$. The form of Eq. (2.81) is known as the *Kraus representation* - or operator sum representation - and is the general structure of a dynamical map, where the operators $\{\hat{K}^{(1)}_{\beta\alpha}(t,t_0), \beta, \alpha = 1, ..., d^{(2)}\}$ are the *Kraus operators.* In particular, if there is only one Kraus operator $\hat{K}^{(1)}_j(t,t_0)$, then the map simplifies to $\hat{\Lambda}^{(1)}_{t,t_0}\hat{\rho}^{(1)}(t_0) = \hat{K}^{(1)}_j(t,t_0)\hat{\rho}^{(1)}(t_0)\hat{K}^{(1)\dagger}_j(t,t_0)$ and the time evolution is unitary, since $\hat{K}^{(1)\dagger}_j(t,t_0)\hat{K}^{(1)}_j(t,t_0) = \hat{1}^{(1)}$.

In short, the dynamics of open systems are considerably more complicated than the isolated and closed ones and require a more general approach for treating them. As mentioned earlier, in realistic scenarios, any object is unavoidable coupled to its external environment. Its interactions often lead to an intricate non-unitary time evolution that is not easily described by analytic means. In this sense, all the formalism and approximations developed within the context of open quantum systems are useful tools for understanding the behaviour of interacting systems.

2.3 Quantum thermodynamics

Given the previous introductions from Sections (2.1) and (2.2), it is clear that thermodynamics and quantum mechanics are both successful and well established physical theories developed and applied to different aspects of natural phenomena. However, it is not a priori obvious to understand how they connect. The research program coined as *quantum thermodynamics* (QT) is relatively young and has been emerging as a meaningful scientific field during the last couple of decades. Its name is self-explanatory[w] since QT has the ambition to develop a consistent theory that both extends and applies thermodynamics for general, and possibly nonequilibrium, quantum systems and to describe the classical thermodynamic behaviour from the underlying fundamental quantum dynamics. Both major goals are clearly complementary and represent different valid perspectives on the same subject, which partially explains the diverse community forming around QT and the plethora of approaches and ideas coming from distinct - but closely related - areas, especially from quantum information theory and open quantum systems. For a general introduction to this topic, see. (42–46) A more detailed discussion on QT can be found in. (47–49)

Although the recent impressive booming of the field, it is interesting to notice that, historically, thermodynamics has always been assisting quantum mechanics. In fact, it was present at the birth of quantum theory (50, 51) and, during the last century, supported some crucial technological advances, in particular in the development of the lasers and masers. (52–55) However, despite being centenary theories, it is no surprise, nor coincidence, that questions concerning the thermodynamics of quantum systems have been rapidly coming to light during present days: On the one hand, since the early 90s seminal results on nonequilibrium thermodynamics (16–19, 21), the field of stochastic thermodynamics flourished and has been successfully bridging the gap between the understanding of macroscopic and microscopic thermodynamic processes (10, 12); On the other hand, the current state-of-the-art technology allows the precise fabrication, control and measurement of truly quantum objects in a wide variety of platforms, ranging from solid-state systems to trapped ions and optical setups. In this context, questions concerning whether or not it is possible to expand the laws of thermodynamics to even smaller - and possibly quantum - systems is both a logical step and a current technological urgency. In fact, along with quantum computation and quantum information, QT is an important player in the contemporary technological revolution, the so-called *quantum technologies 2.0*. Its primary purpose is to design quantum devices capable of intentionally harvesting quantum properties, such as coherence and entanglement, to outperform their classical counterparts and - hopefully - execute functions that no classical machines could do, even in principle. At the core of these technologies, it is necessary to understand the underlying interplay between work, heat and information. On this wise, QT provides the most natural framework to deal with the design and manipulation of quantum heat engines (53, 55–67), which is a fundamental step toward the development of efficient and stable functioning quantum machines. However, it is important to emphasize that, to this date, it is still

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[w] Interestingly, this is not the case for many things in science.

not clear to what extent such kinds of devices would be feasible in practical scenarios. Physicists are optimistic, though. Currently, QT investigations are already accessible and performed in the traditional experimental setups for quantum mechanics studies, e.g., superconducting devices (68–76), nitrogen-vacancy (NV) centers (77, 78), nuclear magnetic resonance (NMR) (79–82), trapped ions (83–86), ultracold atoms (87–89) and others. In this sense, much experimental research in QT is driven by questions concerning cyclic processes, quantum heat engines and quantum refrigerators. (77, 80, 81, 84–86, 90) For more details and further references, see. (91) Additionally, from a theoretical perspective, QT has the potential to shed some light on fundamental questions on the foundations of quantum mechanics and statistical physics, especially those concerning the emergence of macroscopic behaviour from first principles, e.g., the transition from quantum to classical mechanics, irreversibility, thermalisation and the measurement problem.

As briefly mentioned earlier, QT has been approached from many different perspectives and attitudes, each one tackling particular problems with its own set of tools. This diversity gave rise to smaller communities and several research branches within QT. Along these lines, in addition to studies with quantum heat engines, one can find investigations on quantum thermometry (92–98), quantum batteries (99–103), stochastic quantum thermodynamics (104–109) and thermodynamics of quantum information (71, 110–114), just to name a few. All these subareas have been reporting interesting and relevant theoretical progress, although not in a cohesive manner yet. In particular, pertinent developments are being achieved by resource theoretic notions imported from quantum information theory and applied to QT. (115–120) Resource theories are robust axiomatic and operational mathematical descriptions of the so-called *resources* and *free operations*: while the former refers to desired - and possibly scarce (just like any resource) - physical properties, like entanglement and coherence, the latter refers to the set of feasible and accessible operations. Interestingly, using this framework, one can derive general results concerning possible state transformation under a given set of constraints. At present, there is a plethora of different resource theories, each one dealing with its particular resources and set of operational restrictions. (121, 122) In the thermodynamic context, nonequilibrium states are seen as resources, while free operations include the addition of thermal baths and global unitaries preserving energy. (123, 124) It is interesting to appreciate how similar such reasoning is compared with the usual phenomenological approach to thermodynamics.

Alternatively, instead of knowing whether or not a given transformation is possible, one might be interested in the process itself (125, 126), i.e., in all the dynamical aspects within a time-dependent transformation, which certainly includes both energetic and entropic changes. In this sense, describing the dynamics of any desired property in a given protocol is of fundamental importance for a complete quantum thermodynamic theory. Furthermore, such knowledge is clearly necessary for technological applications where is expected a high degree of control during the preparation and manipulation of sophisticated and fragile quantum states. In fact, the most promising - and interesting - applications will demand local descriptions of interacting quantum systems, especially when dealing with quantum heat engines and contexts like quantum control and quantum sensing. For these reasons, the framework of open quantum systems (40) is a natural - and unavoidable - candidate to approach quantum thermodynamics and has been extensively used in several contexts. Along these lines, both the understanding of open quantum systems and the tools used to describe them are slowly pushing the usual orthodox thermodynamic scenario to a wide range of situations.

Given the relatively young age of QT, there is no surprise to notice the presence of several open problems. In fact, considering its stage, this is expected. However, despite all current advances and efforts, the lack of consensus on central aspects of the theory is particularly notorious. This situation can be explained, at least partially, by the still unknown thermodynamic role of quantum properties, i.e., once considered interacting quantum systems, subtleties concerning entanglement, coherence, and the interaction should be carefully scrutinized. Of course, classical thermodynamics give us some expectations of how things should occur. Nevertheless, such properties vanish at the appropriate classical limit: while genuine quantum phenomena are absent in any classical setting, the interaction is negligible for macroscopic systems. In this sense, (remarkably) there is still no acceptable *general* definitions for the quantum counterparts of the most basic thermodynamic quantities, which highlights the need for further investigations at the foundational and conceptual levels.

Along these lines, the obtention of a general quantum thermodynamic entropy remains elusive. Different alternatives can be found in the literature (127–131), but, unsurprisingly, most current approaches are based on information-theoretic perspectives. (132) Despite its success for microscopic classical systems (133) and particular - orthodox - quantum scenarios (56, 134), it does not satisfy the expected properties for a proper generalization of thermodynamic entropy and the second law. Unfortunately, this is also the case for internal energy and the first law. There is no ambiguity in identifying the internal energy of isolated quantum systems, i.e., this role is unambiguously assigned to the expectation value of its Hamiltonian. However, it is not clear how to proceed once considering arbitrary open quantum systems. In such cases, the notion of physical local internal energy is clouded by existing non-negligible interactions and correlations between the system of interest and its surroundings. Naturally, any attempt description of energy exchanges inherits such basic dubiety. In this sense, classical thermodynamics states that energy flow is divided into two complementary and fundamentally distinct categories, work and heat. Such splitting for the quantum case also carries some intrinsic difficulties. As mentioned earlier in Section (2.1.1), work and heat are defined along with trajectories, which establish an extra conceptual barrier for directly translating them to the quantum realm. (135) More importantly, it is uncertain how to account for the energetic contributions of coherence and quantum correlations into these elements. Still, most of the current strategies are grounded on the classical - and pragmatical - reasoning that work is associated with the energy transferred in a controllable and deterministic fashion via the precise control of external parameters, and heat is linked to randomly exchanged energy during a given process and entropic variation. This perspective has been explored in different ways and with distinct frameworks. On the one hand, many efforts were driven by the quest for the quantum versions of FTs and measurement-based approaches. (104, 105, 136) On the other hand, a fully quantum dynamic description is also sought from a less operational point of view. (56, 125, 126) Interestingly, it should be emphasized that despite all the above discussion, even the usual assumption of splitting the energy flow solely in terms of work and heat can be debatable for the quantum case. (137)

Additionally, another critical aspect concerns the enormous difficulty of describing the dynamics of open quantum systems. As briefly mentioned in the overview of Section (2.2.2.2), the time-evolution of reduced states may be extremely convoluted and rarely solvable exactly. Besides, unless we are dealing with simple physical systems, this type of description and analysis is a formidable task, even for numerical methods. Thus, most procedures assume several approximations for microscopically deriving more tractable dynamical equations, which inevitably restrains its validity for specific conditions and scenarios. In particular, it is often considered weak-coupling regimes and Markovian dynamics leading to the usual Lindblad-like form of master equations.[x] (56, 126, 138–142) For more complex situations, when several interacting subsystems are being described, alternative approaches also consider the so-called local master equations by strategically neglecting some interaction terms, which simplifies the analysis even further. (143, 144) Nevertheless, these approximations can lead to thermodynamic inconsistency or unphysical situations when not taken into account carefully. (145–149) Alternatively, it was recently shown the possibility to derive thermodynamically compatible master equations by employing additional selective hypotheses. (150) However, it is clear that relying on approximations and other restrictive assumptions also poses a critical limitation to the development of a general thermodynamic description of quantum systems, especially if one intends to characterize strongly-coupled systems and further arbitrary contexts. In this sense, there are efforts to extend the usual approach for broader scenarios. (109, 151–164)

In addition to the approximate treatment commonly employed in QT, a semi-classical description is also implicitly assumed, i.e., although not usually highlighted, the addition of a classical external agent is a fundamental part of the standard formalism, especially for closed quantum systems. Essentially, this agent is responsible for controlling the dynamics of the system of interest and inducing its Hamiltonian time-dependency, which yield the energy exchange directly interpreted as work. It is also the relevant party

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[x] In the literature, it is also commonly referred to as Gorini, Kossakowski, Lindblad, and Sudarshan (GKLS) equation.

for measuring the system and, eventually, processing the accessible information. From a physical point of view, this control is mediated by the use of external fields interacting with the system in question in such a way that it maintains its quantum properties. However, they are not explicitly included in the physical description. Instead, they are regarded as classical fields whose interaction induces an effective time-dependency in the system's Hamiltonian. Despite its practical relevance, this perspective of the so-called "coherent control" (165) does not contemplate autonomous quantum systems and, therefore, limits ourselves to the thermodynamic description of classically driven devices, where both the quantum nature of the fields is unimportant relative to the system of interest and the system itself does not affect the control's state. In contrast to a semi-classical approach, autonomous quantum systems are isolated and do not have Hamiltonian time-dependency, which means that all relevant parties - including the control agent - are quantized. Of course, it also implies that the semi-classical description is a limit regime. Along with this more general and fundamental picture, one is interested in understanding the thermodynamics *within* isolated quantum systems, which would enable the design and characterization of autonomous quantum machines. In this sense, any attempt of developing a thermodynamic description of quantum systems that assumes a time-dependent Hamiltonian a priori is not fully quantum and, essentially, a phenomenological approach. Interestingly, this fundamental - and conceptual - issue is not mentioned very often in the literature of QT. For some discussions on autonomous quantum machines, see. (166–181) More recently, (182) presented a formal treatment (although restricted to the usual thermodynamic scenario) on this topic. It is worth mentioning that these questions are also at the heart of quantum (optimal) control theory. See (183–186) for more discussions on this matter.

Finally, the recent global interest in developing a quantum thermodynamic theory is growing fast each year. The contemporary version of the industrial revolution is spearheaded by current progress in understanding and developing genuine quantum technologies for information processing, communication and sensing. In this context, a fully matured framework of QT will certainly play a leading role in the design and operation of functional quantum devices. Nevertheless, despite being a promising field, considering its actual stage of achievements and open questions, it is still in its infancy. More specifically, additional investigations are needed at the conceptual level, as several fundamental aspects are still under scrutiny. In short, QT is an interesting, stimulating and young research field whose investigations and potential scientific breakthroughs will, in one way or another, help to shape future technologies and the understanding of quantum mechanics. Hopefully, future historians of physics will view this chapter of science as we see past developments today.

3 SCHMIDT DECOMPOSITION APPROACH TO QUANTUM THERMODYNAMICS

In Section (2.3), we briefly introduced the current efforts and growing progress on the development of a self-consistent thermodynamic theory of quantum systems. Despite clear advancements toward this goal, the field of quantum thermodynamics (QT) still has some fundamental issues to be addressed. In this sense, most theoretical frameworks inherit some of the phenomenological spirit of the classical theory and do not provide suitable tools to characterize and understand thermodynamic processes within genuine autonomous quantum machines, i.e., most modern approaches are built on the top of semi-classical descriptions and approximative regimes, which clearly limit their range of applicability.

In this chapter, we are interested to address and contribute to such more foundational aspects of the theory. In the following pages, we are going to present a novel approach to the thermodynamic analysis of autonomous quantum systems. Our proposal is exact and based on the well-known procedure of the Schmidt decomposition for bipartite systems[a]. Interestingly, despite being simple and providing a powerful statement, it is still not explicitly explored in the context of QT. This framework will allow us to describe the dynamics and energetics within generic interacting subsystems in a symmetrical fashion, i.e., regardless of their individual properties, details and dimension, they will be treated on equal footing. In addition, it will not require any complementary hypotheses and approximations, such as the commonly used ones concerning the Hamiltonian structure, interaction regimes and type of dynamics, i.e., strict energy conservation, weak-coupling, markovianity, etc. Formally, we will introduce time-dependent local effective Hamiltonians that naturally embrace both their respective bare ones and the contributions of the interaction term. These elements will be identified as the representative operators for characterizing the subsystem's physical internal energies, in a way that will allow us to extend the usual classical thermodynamic notion of energy additivity to general interacting quantum systems[b].

The outline of this chapter is the following: Section (3.1) formally introduces and details the main setup of analysis, which consists of an isolated pure bipartite quantum system. Also, it establishes the mathematical notation used throughout the chapter. Then, Section (3.2) presents the foundations of our formalism. More specifically, it discusses and describes the Schmidt basis dynamics and identifies their time-translation generators as

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[a] Or single systems where there is coupling between diferent degrees of freedom, e.g., spin-orbit interaction.

[b] The following main discussions and results can be found in (1), submitted after this thesis defense.

the so-called local effective Hamiltonians. The following Section (3.3) briefly mentions how the local dynamics are represented relative to these operators and the Schmidt basis/coefficients. Then, in Section (3.4), the notion of local internal energies is discussed in the context of QT. Also, it is argued that the effective operators previously defined are suitable candidates for characterizing the subsystem's physical internal energy. Along these lines, Section (3.5) introduces and discusses the consequences of the intrinsic phase/frame gauge degree of freedom underlying the Schmidt decomposition and, therefore, inherited by our formalism. More importantly, it is presented a procedure for fixing it. Section (3.6) focuses on the analysis of current approaches for defining quantum versions of thermodynamic quantities. After that, Section (3.7) shows a proof of principle of the proposed formalism. Then, Section (3.8) generalizes the previous results to mixed bipartite states. And, finally, Section (3.9) briefly discusses these results and summarizes the chapter.

3.1 The setting

As mentioned earlier, we consider a finite, isolated and nondegenerate pure quantum system composed of two smaller interacting subsystems. Throughout this thesis, the whole system and its global quantities will be labelled by (0), while the parts and their relative local properties will be identified by (1) and (2). Let $\mathcal{H}^{(k)}$, with $k = 0, 1, 2$, be their Hilbert spaces with dimensions $d^{(k)} := dim(\mathcal{H}^{(k)})$, such that $d^{(0)} = (d^{(1)} + d^{(2)})$ and - without any loss of generality - $d^{(1)} \leq d^{(2)}$. Since we are interested in describing a fully quantum autonomous object, the whole system Hamiltonian $\hat{H}^{(0)}$ generating its dynamics is time-independent and given by

$$\hat{H}^{(0)} := \hat{H}^{(1)} \otimes \hat{1}^{(2)} + \hat{1}^{(1)} \otimes \hat{H}^{(2)} + \hat{H}_{int}, \tag{3.1}$$

where $\hat{1}^{(1,2)} \in \mathcal{L}(\mathcal{H}^{(1,2)})$ are the identity operators, $\hat{H}^{(1,2)} \in \mathcal{L}(\mathcal{H}^{(1,2)})$ are the local bare Hamiltonians of each subsystem and $\hat{H}_{int} \in \mathcal{L}(\mathcal{H}^{(0)})$ is the term that encompasses all the internal interactions between them. It is important to emphasize that no additional hypothesis will be considered, especially concerning dynamical features or the Hamiltonian/interaction structure, e.g., markovianity, uncorrelated states, weak coupling, specific interaction Hamiltonian, etc. The following description is general and exact.

At any time t the whole pure system is described by a ket $|\Psi(t)\rangle \in \mathcal{H}^{(0)} = \mathcal{H}^{(1)} \otimes \mathcal{H}^{(2)}$. Besides, since it is isolated, its dynamics is governed by the usual Schrödinger equation $i\hbar\frac{d}{dt}|\Psi(t)\rangle = \hat{H}^{(0)}|\Psi(t)\rangle$; thereby, for any initial state $|\Psi(t_0)\rangle$ and $t \geq t_0$ we have

$$|\Psi(t)\rangle = \hat{\mathcal{U}}(t, t_0)|\Psi(t_0)\rangle, \tag{3.2}$$

where $\hat{\mathcal{U}}(t, t_0) = e^{-\frac{i}{\hbar}\hat{H}^{(0)}(t-t_0)} \in \mathcal{L}(\mathcal{H}^{(0)})$ is the time-evolution operator of the whole. As usual, such bipartite state could be written in any conceivable basis, e.g., $|\Psi(t)\rangle = \sum_{i=1}^{d^{(1)}} \sum_{j=1}^{d^{(2)}} \psi_{ij}(t)|b_i^{(1)}, b_j^{(2)}\rangle$, nevertheless the well known Schmidt decomposition guarantee the following specific and convenient form (see (2.2.1.3.1))

$$|\Psi(t)\rangle = \sum_{j=1}^{d^{(1)}} \lambda_j(t)|\varphi_j^{(1)}(t)\rangle \otimes |\varphi_j^{(2)}(t)\rangle, \tag{3.3}$$

for every instant t, where $\{\lambda_j(t) \geq 0; j = 1, ..., d^{(1)}\}$ and $\{|\varphi_j^{(k)}(t)\rangle; j = 1, ..., d^{(1)}\}$[c]$\in \mathcal{H}^{(k)}$ are the time-local Schmidt coefficients and local Schmidt basis of subsystem (k), respectively. The normalization condition $\langle\Psi(t)|\Psi(t)\rangle = 1$ implies that $\sum_{j=1}^{d^{(1)}} \lambda_j^2(t) = 1$, and the orthonormality of the local basis elements assure that $\langle\varphi_m^{(\alpha)}(t)|\varphi_n^{(\beta)}(t)\rangle = \delta_{\alpha\beta}\delta_{mn}$. From now on, the Schmidt decomposition form showed in Eq. (3.3) will be the standard description of $|\Psi(t)\rangle$.

As already mentioned in chapter (2), the representation above is compelling and useful for a number of reasons: notice that despite a potential huge discrepancy between $d^{(1)}$ and $d^{(2)}$ there is a single sum bounded by the smallest dimension in question, by hypothesis $d^{(1)}$[d]; apart from that, it is symmetrical in the sense that for each ket $|\varphi_j^{(1)}(t)\rangle$ from subsystem (1) there is a related ket $|\varphi_j^{(2)}(t)\rangle$ from (2); additionally, as we are going to present below, it turns out that it gives all necessary information for representing the subsystem's local states; also, it is guaranteed that the Schmidt coefficients are unambiguously defined, while the Schmidt basis are unique up to eventual degenerate coefficients and a phase degree of freedom, in the sense that Eq. (3.3) is invariant over simultaneous local phases changes (this point will be discussed later in Section (3.5)); finally, it makes easy to verify whether the subsystems are entangled or not, i.e., a product state will be obtained iff there is a single non-zero Schmidt coefficient[e] such that $\lambda_j(t) = 1$, $\lambda_m(t) = 0$ for all $m \neq j$ and $|\Psi(t)\rangle = |\varphi_j^{(1)}(t)\rangle \otimes |\varphi_j^{(2)}(t)\rangle$. As a last remark, it is important to highlight the fact that the set $\{|\varphi_j^{(2)}(t)\rangle\}_j$ of Schmidt basis is not formally complete since we only have $d^{(1)}$ elements, still we are always allowed to find the remaining $(d^{(2)} - d^{(1)})$ orthonormal kets to form a complete basis of $\mathcal{H}^{(2)}$.

Let us now turn our attention to the parts: the individual state description of each subsystem is represented by the reduced density matrix of the whole, whose own pure state density matrix is

$$\hat{\rho}^{(0)}(t) \equiv |\Psi(t)\rangle\langle\Psi(t)|. \tag{3.4}$$

Formally, these local states are obtained by the usual procedure of partial tracing Eq. (3.4) such that $\hat{\rho}^{(1,2)}(t) \equiv tr_{2,1}\{\hat{\rho}^{(0)}(t)\}$. Thus, given Eq. (3.3) it is easy to see that, for all

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[c] Unless it is necessary, from now on, any set will be represented simply as $\{a_j\}_j$ where j is the index counting its elements, and the range is implicit.

[d] Even though the sum extends up to $d^{(1)}$ we may have null Schmidt coefficients thus, in practice, the sum goes until the Schmidt rank, defined as the number of non-zero coefficients. To keep track of these dimensions, we will maintain $d^{(1)}$ in the sums.

[e] Schmidt rank equal to one.

t,

$$\hat{\rho}^{(1)}(t) = \sum_{j=1}^{d^{(1)}} \lambda_j^2(t) |\varphi_j^{(1)}(t)\rangle\langle\varphi_j^{(1)}(t)|, \tag{3.5}$$

$$\hat{\rho}^{(2)}(t) = \sum_{j=1}^{d^{(1)}} \lambda_j^2(t) |\varphi_j^{(2)}(t)\rangle\langle\varphi_j^{(2)}(t)|. \tag{3.6}$$

Hopefully, the expressions above are sufficient to further elucidate how convenient the Schmidt decomposition really is. As briefly mentioned earlier, its provides all necessary information for inferring the spectral decomposition of these states, i.e., their eigenvalues (also referred as populations) and eigenvectors are given by the Schmidt coefficients squared $\{\lambda_j^2(t)\}_j$ and Schmidt basis $\{|\varphi_j^{(1,2)}(t)\rangle\}_j$, respectively. In particular, notice that both local states are represented - in general - by mixed density matrices[f] and necessarily have the same spectrum whenever the whole bipartite system is pure; more precisely, since $d^{(2)} \geq d^{(1)}$ the spectrum of subsystem (2) cointains the set $\{\lambda_j^2(t)\}_j$ plus $(d^{(2)} - d^{(1)})$ null eigenvalues, whose respective eigenvectors form the nullspace of $\hat{\rho}^{(2)}(t)$[g]. Additionally, this also implies that both subsystems will have the same values for any local functional of their populations, most notably purity and von-Neumann entropy.

3.2 Schmidt basis dynamics and local effective Hamiltonians

In this section, we are particularly interested in a *local* dynamical description of the Schmidt basis $\{|\varphi_j^{(1,2)}(t)\rangle\}_j$, whereas by local we mean a description solely based in terms relative to their respective Hilbert space $\mathcal{H}^{(1,2)}$. Firstly, it is important to emphasize that both sets of Schmidt coefficients and pair of basis are intrinsically connected to the whole system state, in the sense that for every ket $|\Psi(t)\rangle$ there is a single decomposition. Having that in mind, a pictorial representation might by useful: at any time interval $[t_0, t_1]$ the autonomous time evolution performed by the whole can be visualized as a curve $\mathcal{P}^{(0)} : |\Psi(t)\rangle,\ t \in [t_0, t_1]$ in the total Hilbert space $\mathcal{H}^{(0)}$; nevertheless, given Eq. (3.3) such path can be mapped into the simultaneous coupled trajectories $\mathcal{P}_j^{(1,2)} : |\varphi_j^{(1,2)}(t)\rangle,\ t \in [t_0, t_1]$ followed by the Schmidt basis in their own Hilbert spaces, and the paths of the Schmidt coefficients, $\mathcal{P}_j^{\lambda} : \lambda_j(t) \geq 0, t \in [t_0, t_1]$, such that $\lambda_j^2(t) \in [0, 1]$ for all j, and $\sum_{j=1}^{d^{(1)}} \lambda_j^2(t) = 1$. Obviously, once one has access to the initial state $|\Psi(t_0)\rangle$, $\mathcal{P}^{(0)}$ is fully characterized by the unitary operator $\hat{\mathcal{U}}(t, t_0)$ and Eq. (3.2), while the correlated behaviours of $\{\mathcal{P}_j^{(1,2)}\}_j$ and $\{\mathcal{P}_j^{\lambda}\}_j$ are direct byproducts of the former. For instance, at any time t we have the following expression for the coefficients

$$\lambda_j(t) = \sum_{k=1}^{d^{(1)}} \lambda_k(t_0) \langle\varphi_j^{(1)}(t), \varphi_j^{(2)}(t)|\hat{\mathcal{U}}(t, t_0)|\varphi_k^{(1)}(t_0), \varphi_k^{(2)}(t_0)\rangle, \tag{3.7}$$

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[f] Iff the Schmidt rank is equal to one we have non-entangled systems and pure local states.

[g] Obviously, if $d^{(2)} > d^{(1)}$ the density matrix $\hat{\rho}^{(2)}(t)$ is automatically singular.

where it clearly depends on the initial state of the whole, its time-evolution operator and the instantaneous Schmidt basis. However, such global knowledge is rarely accessible in most realistic scenarios, thus what we are really interested in is to inferring and describing the individual effective dynamics portrayed by $\mathcal{P}_j^{(1,2)}$ such that defining *local* thermodynamic quantities is meaningful and universal, in the sense that the theoretical machinery can be applied for both parts without any further adjustments. Such a procedure will prove very useful in describing the subsystems dynamics and their energetic flux.

Let us now put it more formally: initially, we define the local dynamical map $\tilde{\mathcal{U}}^{(k)} : \mathcal{H}^{(k)} \to \mathcal{H}^{(k)}$ $(k = 1, 2)$ that serves as a time-evolution operator and reproduces the paths $\{\mathcal{P}_j^{(k)}\}_j$ in a way that every Schmidt basis ket continuously follows

$$|\varphi_j^{(k)}(t)\rangle = \tilde{\mathcal{U}}^{(k)}(t, t_0)|\varphi_j^{(k)}(t_0)\rangle, \tag{3.8}$$

for any $t \geq t_0$, with $\underset{t\to t_0}{lim}|\varphi_j^{(k)}(t)\rangle = |\varphi_j^{(k)}(t_0)\rangle$ or $\underset{t\to t_0}{lim}\tilde{\mathcal{U}}^{(k)}(t, t_0) = \hat{1}^{(k)}$. Since the Schmidt basis at distinct times corresponds to a different orthonormal basis for the same Hilbert space, the relationship above is trivially guaranteed[h]. Additionally, it is required both that

$$\langle\varphi_l^{(k)}(t)|\varphi_j^{(k)}(t)\rangle = \langle\varphi_l^{(k)}(t_0)|\varphi_j^{(k)}(t_0)\rangle = \delta_{lj}, \tag{3.9}$$

and

$$\tilde{\mathcal{U}}^{(k)}(t_2, t_0) = \tilde{\mathcal{U}}^{(k)}(t_2, t_1)\tilde{\mathcal{U}}^{(k)}(t_1, t_0), \tag{3.10}$$

for $t_2 > t_1 > t_0$, where the former condition guarantees the orthonormality during the entire dynamics, and the latter demands the composition of the maps for intermediate times. It is worth mentioning that, in general, these local maps are not directly related to the whole time-evolution operator, such that $\hat{\mathcal{U}}(t, t_0) \neq \tilde{\mathcal{U}}^{(1)}(t, t_0) \otimes \tilde{\mathcal{U}}^{(2)}(t, t_0)$. The previous conditions are automatically fulfilled if the time evolution operator $\tilde{\mathcal{U}}^{(k)}(t, t_0)$ is unitary, i.e., $\tilde{\mathcal{U}}^{(k)\dagger}(t, t_0)\tilde{\mathcal{U}}^{(k)}(t, t_0) = \hat{1}^{(k)}$, and have the form presented below for infinitesimal temporal displacements dt,

$$\tilde{\mathcal{U}}^{(k)}(t + dt, t) = \hat{1}^{(k)} - \frac{i}{\hbar}\tilde{H}^{(k)}(t)dt, \tag{3.11}$$

where $\tilde{H}^{(k)}(t) = \tilde{H}^{(k)\dagger}(t) \in \mathcal{L}(\mathcal{H}^{(k)})$ is a hermitian and possibly time-dependent operator. Thus, one can show that

$$i\hbar\frac{d}{dt}\tilde{\mathcal{U}}^{(k)}(t, t_0) = \tilde{H}^{(k)}(t)\tilde{\mathcal{U}}^{(k)}(t, t_0), \tag{3.12}$$

and, therefore,

$$i\hbar\frac{d}{dt}|\varphi_j^{(k)}(t)\rangle = \tilde{H}^{(k)}(t)|\varphi_j^{(k)}(t)\rangle, \tag{3.13}$$

for all j. The Eq. (3.13) describes exactly what we wanted, where the new operator $\tilde{H}^{(k)}(t)$ introduced above plays the role of the time-translation generator of the Schmidt

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[h] In fact, we already know it should be unitary.

basis $\{|\varphi_j^{(k)}(t)\rangle\}_j$ along with $\{\mathcal{P}_j^{(k)}\}_j$, and, from now on, will be referred to as the *local effective Hamiltonian* of subsystem (k).

Now, the most natural question is "What exactly is the form of $\tilde{H}^{(k)}(t)$?". It certainly should depend on the context, in the sense that different initial conditions will give rise to distinct Schmidt basis trajectories and, therefore, a new effective Hamiltonian. In fact, this is clear once noticed that the equality above can be reversed such that

$$\tilde{H}^{(k)}(t) \equiv i\hbar \sum_{j=1}^{d^{(k)}} \frac{d}{dt}|\varphi_j^{(k)}(t)\rangle\langle\varphi_j^{(k)}(t)|, \tag{3.14}$$

in other words, knowing the Schmidt basis and its dynamics one could obtain its respective local effective Hamiltonian. Interestingly, despite this convoluted nature with the whole pure quantum system state, such operator is locally accessible in principle, since the Schmidt basis are exactly the eigenbasis of the local state $\hat{\rho}^{(k)}(t)$ in question. Nevertheless, we can go one step further and show that Eq. (3.14) can be directly related to the local bare Hamiltonian $\hat{H}^{(k)}$. To do so, we first explicitly write down the latter in its spectral decomposition

$$\hat{H}^{(k)} \equiv \sum_{j=1}^{d^{(k)}} b_j^{(k)}|b_j^{(k)}\rangle\langle b_j^{(k)}|, \tag{3.15}$$

where $\{b_j^{(k)}\}_j$ and $\{|b_j^{(k)}\rangle\}_j$ are its respective bare eigenenergies and eigenbasis. Then we define the projection $\langle b_j^{(k)}|\varphi_l^{(k)}(t)\rangle := r_{jl}^{(k)}(t)e^{-\frac{i}{\hbar}b_j^{(k)}t}$, in such a way that

$$\langle b_j^{(k)}|\frac{d}{dt}|\varphi_l^{(k)}(t)\rangle = \left(\frac{d}{dt}r_{jl}^{(k)}(t)\right)e^{-\frac{i}{\hbar}b_j^{(k)}t} - \frac{i}{\hbar}b_j^{(k)}r_{jl}^{(k)}(t)e^{-\frac{i}{\hbar}b_j^{(k)}t}. \tag{3.16}$$

Besides, given the basis orthonormality $\langle b_\alpha^{(k)}|b_\beta^{(k)}\rangle = \delta_{\alpha\beta}$, we also have

$$\sum_{l=1}^{d^{(k)}} r_{\alpha l}^{(k)}(t)\left(r_{\beta l}^{(k)}(t)\right)^* e^{\frac{i}{\hbar}\left(b_\beta^{(k)}-b_\alpha^{(k)}\right)t} = \delta_{\alpha\beta}. \tag{3.17}$$

Finally, by casting $\tilde{H}^{(k)}(t)$ in the bare eigenbasis representation and using the previous relations, one can rewrite the local effective Hamiltonian as follows

$$\tilde{H}^{(k)}(t) = \hat{H}^{(k)} + \hat{H}_{LS}^{(k)}(t) + \hat{H}_X^{(k)}(t), \tag{3.18}$$

where

$$\hat{H}_{LS}^{(k)}(t) := i\hbar\sum_{j=1}^{d^{(k)}}\left(\sum_{l=1}^{d^{(k)}}\left(\frac{d}{dt}r_{jl}^{(k)}(t)\right)r_{jl}^{(k)*}(t)\right)|b_j^{(k)}\rangle\langle b_j^{(k)}|, \tag{3.19}$$

$$\hat{H}_X^{(k)}(t) := i\hbar\sum_{j=1}^{d^{(k)}}\sum_{m\neq j}^{d^{(k)}}\left(\sum_{l=1}^{d^{(k)}}\frac{d}{dt}r_{jl}^{(k)}(t)r_{ml}^{(k)*}(t)\right)e^{\frac{i}{\hbar}\left(b_m^{(k)}-b_j^{(k)}\right)t}|b_j^{(k)}\rangle\langle b_m^{(k)}|. \tag{3.20}$$

Thus, the local effective Hamiltonian can be split into the sum of three distinct elements, including the bare Hamiltonian. Note that the additional operators are responsible for the time-dependency of $\tilde{H}^{(k)}(t)$, where $\hat{H}_{LS}^{(k)}(t)$ is a general Lamb-shift like term, in the sense that it is diagonal in the bare eigenbasis, i.e., $[\hat{H}_{LS}^{(k)}(t), \hat{H}^{(k)}] = 0$ for all t, and $\hat{H}_{X}^{(k)}(t)$ contains only non-diagonal elements. Intuitively, such extra quantities are expected to be somehow related to the interaction term. Notice that in its absence, each subsystem would unitarily evolve in time according to their individual bare Hamiltonians, since $\hat{\mathcal{U}}(t, t_0) = e^{-\frac{i}{\hbar}\hat{H}^{(0)}(t-t_0)} = e^{-\frac{i}{\hbar}\hat{H}^{(1)}(t-t_0)}e^{-\frac{i}{\hbar}\hat{H}^{(2)}(t-t_0)}$ for this scenario. Thus, for a initial state $|\Psi(t_0)\rangle$ we would have

$$|\Psi(t)\rangle_{bare} = \sum_{j=1}^{d^{(1)}} \lambda_j(t_0)|\varphi_j^{(1)}(t)\rangle_{bare} \otimes |\varphi_j^{(2)}(t)\rangle_{bare}, \tag{3.21}$$

where $|\varphi_j^{(k)}(t)\rangle_{bare} = e^{-\frac{i}{\hbar}\hat{H}^{(k)}(t-t_0)}|\varphi_j^{(k)}(t_0)\rangle$ represents the free evolution of the initial Schmidt basis, for $t \geq t_0$. Hence, in this case, the Schmidt coefficients $\{\lambda_j(t_0)\}_j$ are constant and the local effective Hamiltonians are simply identified as the bare ones, i.e, $\tilde{H}^{(k)}(t) = \hat{H}^{(k)}$. This, however, can be seen from the usual time-independent theory approach. Let us now add a dimensionless parameter $\varepsilon \in [0, 1]$ and make $\hat{H}_{int} \to \varepsilon\hat{H}_{int}$, such that we can write the following formal perturbative series

$$\lambda_j(t) = \lambda_j(t_0) + \varepsilon\lambda_{j,1}(t) + \mathcal{O}_\lambda(\varepsilon^2), \tag{3.22}$$

$$|\varphi_j^{(k)}(t)\rangle = |\varphi_j^{(k)}(t)\rangle_{bare} + \varepsilon|\varphi_j^{(k)}(t)\rangle_1 + \mathcal{O}^{(k)}(\varepsilon^2), \tag{3.23}$$

where $\lambda_{j,1}(t)$ and $|\varphi_j^{(k)}(t)\rangle_1$ are the respective first order perturbation elements for the Schmidt coefficients and basis, and $\mathcal{O}_\lambda(\varepsilon^2)$ and $\mathcal{O}^{(k)}(\varepsilon^2)$ are the terms including higher orders corrections. Thus, for sufficiently small ε, the first order approximation for the whole bipartite state is simply

$$|\Psi(t)\rangle \approx |\Psi(t)\rangle_{bare} + \varepsilon|\Psi(t)\rangle_1, \tag{3.24}$$

and, given Eq. (3.14),

$$\tilde{H}^{(k)}(t) \approx \hat{H}^{(k)} + \varepsilon\hat{H}_1^{(k)}(t), \tag{3.25}$$

where $|\Psi(t)\rangle_1$ and $\hat{H}_1^{(k)}$ are their first order components. Hence, any deviation from the bare Hamiltonian is due to the interaction between the subsystems and, as expected, if $\varepsilon \to 0$ it is clear that $\tilde{H}^{(k)}(t) \to \hat{H}^{(k)}$. In short, both additional quantities are the local effective by-products of the interaction term $\hat{H}_{int}$. In fact, later will be shown the functional relationship between their expectation values.

3.3 Local states dynamics

In Section (3.1) we obtained the exact form of the reduced density matrices of our pure bipartite system. We also emphasize how remarkably symmetrical their representation are despite any eventual dimensional difference: we might be dealing with two interacting qubits or a single qubit interacting with a highly complex reservoir, in both scenarios, we would obtain density matrices with equal spectrum, identified by the Schmidt coefficients. Now, we are interested in describing their time-evolution, i.e., to write down the dynamical equation $\frac{d}{dt}\hat{\rho}^{(1,2)}(t)$ for both subsystems.

As a starting point, recall that the whole isolated bipartite system dynamics is unitary and described by the Schrödinger equation. The equivalent description for its density matrix is expressed by the Liouville-von Neumann equation

$$i\hbar\frac{d}{dt}\hat{\rho}^{(0)}(t) = [\hat{H}^{(0)}, \hat{\rho}^{(0)}(t)]. \tag{3.26}$$

Of course, when dealing with the subsystems dynamics such behaviour is not expected, and additional terms should be taken into account to properly describe non-unitary features commonly observed in open quantum systems, e.g., dissipation and decoherence. The first obvious approach for our goal is partial tracing the previous equation and using the total Hamiltonian expression (3.1), such that

$$i\hbar\frac{d}{dt}\hat{\rho}^{(k)}(t) = [\hat{H}^{(k)}, \hat{\rho}^{(k)}(t)] + tr_{\bar{k}}\{[\hat{H}_{int}, \hat{\rho}^{(0)}(t)]\}, \tag{3.27}$$

where $k = 1, 2$, and $\bar{k}$ is its complement (if $k = 1$ we have $\bar{k} = 2$ and vice versa). As we can see, the local time-evolutions are clearly separated into a unitary part, guided by the bare Hamiltonians, and a non-unitary part, represented by the partial trace. Also note that the latter explicitly depends on global properties, represented by the commutation relation between the interaction term and the state of the whole quantum system. It is well known that in some particular scenarios and under specific hypotheses the previous expression can be cast in more relatable forms, usually into time-local master equations with the canonical Lindblad form. Until very recently, a similar simplification for broad dynamics, constraints and initial conditions was elusive, however, S. Alipour *et. al.* (187) showed that the general exact expression for the dynamics of the reduced states, presented in Eq. (3.27), can, in fact, be cast in a universal Lindblad-like form.

Nevertheless, from Eq. (3.13) and the direct derivative of Eqs. (3.5), (3.6) we can write an alternative dynamical expression for both subsystems in terms of their local effective Hamiltonians, and the Schmidt basis and coefficients:

$$i\hbar\frac{d}{dt}\hat{\rho}^{(k)}(t) = [\tilde{H}^{(k)}(t), \hat{\rho}^{(k)}(t)] + i\hbar\sum_{j=1}^{d^{(1)}}\frac{d}{dt}\lambda_j^2(t)|\varphi_j^{(k)}(t)\rangle\langle\varphi_j^{(k)}(t)|. \tag{3.28}$$

Interestingly, by defining the operators $\hat{G}_{\alpha\beta}^{(k)}(t) \equiv |\varphi_\alpha^{(k)}(t)\rangle\langle\varphi_\beta^{(k)}(t)|$ and rates $\gamma_{\alpha\beta}(t) \equiv \frac{1}{d^{(1)}\lambda_\beta^2(t)}\frac{d}{dt}\lambda_\alpha^2(t)$ we can also put it into a non-linear (the rates $\gamma_{\alpha\beta}(t)$ do depend on the state of the whole) Lindblad-like form

$$i\hbar\frac{d}{dt}\hat{\rho}^{(k)}(t) = [\tilde{H}^{(k)}(t), \hat{\rho}^{(k)}(t)] + \hat{\mathfrak{D}}_t^{(k)}\hat{\rho}^{(k)}(t), \tag{3.29}$$

where

$$\hat{\mathfrak{D}}_t^{(k)}\hat{\rho}^{(k)}(t) := i\hbar \sum_{\alpha,\beta=1}^{d^{(1)}} \gamma_{\alpha\beta}(t)\left(\hat{G}_{\alpha\beta}^{(k)}(t)\hat{\rho}^{(k)}(t)\hat{G}_{\alpha\beta}^{(k)\dagger}(t) - \frac{1}{2}\left\{\hat{G}_{\alpha\beta}^{(k)\dagger}(t)\hat{G}_{\alpha\beta}^{(k)}(t), \hat{\rho}^{(k)}(t)\right\}\right). \tag{3.30}$$

In these expressions, the unitary part is governed by the local effective Hamiltonian instead of the bare one, while the non-unitary part explicitly depends on the population time dependency and, therefore, is directly related to the entanglement change during the time evolution. Eq. (3.28) can be seen as a parametric expression for the curve $\mathcal{C}^{(k)} : \hat{\rho}^{(k)}(t)$, $t \in [t_0, t_1]$ followed by the subsystem (k) in its respective density operator space $\mathscr{D}(\mathcal{H}^{(k)})$, such that the unitary contribution is due to the generator of the Schmidt basis paths $\{\mathcal{P}_j^{(k)}\}_j$, and the non-unitary factor is given by the population's trajectories $\{\mathcal{P}_j^{(\lambda)}\}_j$. Thus, it is important to highlight that $\mathcal{C}^{(k)}$ is a byproduct of the whole system dynamics, in the sense that different trajectories $\mathcal{P}^{(0)}$ of $|\Psi(t)\rangle$ originated from distinct initial states, will result in distinct density matrices curves and parametric descriptions.

Finally, since both Eqs. (3.27) and (3.28) are exact expressions for dealing with the same dynamics they can be directly associated. In fact, given Eq. (3.18), both unitary contributions satisfy

$$[\tilde{H}^{(k)}(t), \hat{\rho}^{(k)}(t)] = [\hat{H}^{(k)}, \hat{\rho}^{(k)}(t)] + [\hat{H}_{LS}^{(k)}(t), \hat{\rho}^{(k)}(t)] + [\hat{H}_{X}^{(k)}(t), \hat{\rho}^{(k)}(t)], \tag{3.31}$$

which leads to the following equality for all time t

$$tr_{\bar{k}}\{[\hat{H}_{int}, \hat{\rho}^{(0)}(t)]\} = i\hbar \sum_{j=1}^{d^{(1)}} \frac{d}{dt}\lambda_j^2(t)|\varphi_j^{(k)}(t)\rangle\langle\varphi_j^{(k)}(t)| + [\hat{H}_{LS}^{(k)}(t) + \hat{H}_{X}^{(k)}(t), \hat{\rho}^{(k)}(t)]. \tag{3.32}$$

3.3.1 Unitary dynamics

The previous equations are exact, nevertheless, note that whenever the second term of Eq. (3.28) is negligible compared with the first one, the state dynamics is approximately unitary. Hence, it is valuable to identify - at least qualitatively - what conditions are necessary for having such behaviour. Suppose an arbitrary initial state $|\Psi(t_0)\rangle = \sum_{k=1}^{d^{(1)}} \lambda_k(t_0)|\varphi_k^{(1)}(t_0)\rangle \otimes |\varphi_k^{(2)}(t_0)\rangle$, the Schmidt coefficients at any time t are simply $\lambda_j(t) = \langle\varphi_j^{(1)}(t), \varphi_j^{(2)}(t)|\Psi(t)\rangle$ and

$$\begin{aligned} i\hbar\frac{d}{dt}\lambda_j(t) = {} & \lambda_j(t)\langle\varphi_j^{(1)}(t), \varphi_j^{(2)}(t)|\left(\hat{H}_{int} - \hat{H}_{LSX}^{(1)}(t) - \hat{H}_{LSX}^{(2)}(t)\right)|\varphi_j^{(1)}(t), \varphi_j^{(2)}(t)\rangle \\ & + \sum_{k\neq j}^{d^{(1)}} \lambda_k(t)\langle\varphi_j^{(1)}(t), \varphi_j^{(2)}(t)|\hat{H}_{int}|\varphi_k^{(1)}(t), \varphi_k^{(2)}(t)\rangle, \end{aligned} \tag{3.33}$$

where $\hat{H}_{LSX}^{(k)}(t) := \hat{H}_{LS}^{(k)}(t) + \hat{H}_{X}^{(k)}(t)$ and $\langle\varphi_j^{(1)}(t), \varphi_j^{(2)}(t)|\hat{H}_{int}|\varphi_k^{(1)}(t), \varphi_k^{(2)}(t)\rangle$ with $k \neq j$ are the factors responsible for coupling distinct λ's. If these terms have a minor contribution to the coefficients dynamics, we can write the following approximative solution

$$\lambda_j(t) \approx \lambda_j(t_0)\overleftarrow{\mathcal{T}} e^{-\frac{i}{\hbar}\int_{t_0}^{t} ds\, \langle\varphi_j^{(1)}(s), \varphi_j^{(2)}(s)|\left(\hat{H}_{int} - \hat{H}_{LSX}^{(1)}(s) - \hat{H}_{LSX}^{(2)}(s)\right)|\varphi_j^{(1)}(s), \varphi_j^{(2)}(s)\rangle}, \tag{3.34}$$

where $\overleftarrow{\mathcal{T}}$ is the usual chronological time-ordering operator. However, since $\{\lambda_j(t)\}_j$ are real numbers we must also have

$$\langle\varphi_j^{(1)}(t),\varphi_j^{(2)}(t)|\left(\hat{H}_{int}-\hat{H}^{(1)}_{LSX}(t)-\hat{H}^{(2)}_{LSX}(t)\right)|\varphi_j^{(1)}(t),\varphi_j^{(2)}(t)\rangle=0 \tag{3.35}$$

for all j and t, therefore,

$$\lambda_j(t)\approx\lambda_j(t_0), \tag{3.36}$$

and

$$|\Psi(t)\rangle\approx\tilde{\mathcal{U}}^{(1)}(t,t_0)\tilde{\mathcal{U}}^{(2)}(t,t_0)|\Psi(t_0)\rangle \quad\Rightarrow\quad i\hbar\frac{d}{dt}\hat{\rho}^{(k)}(t)\approx[\tilde{H}^{(k)}(t),\hat{\rho}^{(k)}(t)]. \tag{3.37}$$

Thus, as long as $\langle\varphi_j^{(1)}(t),\varphi_j^{(2)}(t)|\hat{H}_{int}|\varphi_k^{(1)}(t),\varphi_k^{(2)}(t)\rangle\approx 0$ is satisfied for all $j\neq k$ both subsystems evolves approximately unitarily and the degree of entanglement remains conserved. Interestingly, observe that this is true despite the other matrix elements of $\hat{H}_{int}$.

3.3.1.1 Semi-classical external drive

Under the previous approximation, if the initial Schmidt rank is equal to one, such that $|\Psi(t_0)\rangle=|\varphi_\eta^{(1)}(t_0)\rangle\otimes|\varphi_\eta^{(2)}(t_0)\rangle$, we would guarantee uncorrelated local pure states for all t, i.e.,

$$|\Psi(t)\rangle\approx|\varphi_\eta^{(1)}(t)\rangle\otimes|\varphi_\eta^{(2)}(t)\rangle, \tag{3.38}$$

where $|\varphi_\eta^{(k)}(t)\rangle=\langle\varphi_\eta^{(\bar{k})}(t)|\Psi(t)\rangle$ and

$$i\hbar\frac{d}{dt}|\varphi_\eta^{(k)}(t)\rangle\approx(\hat{H}^{(k)}+\langle\varphi_\eta^{(\bar{k})}(t)|\hat{H}_{int}|\varphi_\eta^{(\bar{k})}(t)\rangle-\langle\varphi_\eta^{(\bar{k})}(t)|\hat{H}^{(\bar{k})}_{LSX}(t)|\varphi_\eta^{(\bar{k})}(t)\rangle)|\varphi_\eta^{(k)}(t)\rangle. \tag{3.39}$$

Thus, from Eq. (3.13) it is clear that, in such cases, the local effective Hamiltonian simply becomes

$$\tilde{H}^{(k)}(t)\approx\hat{H}^{(k)}+tr_{\bar{k}}\{(\hat{H}_{int}-\hat{H}^{(\bar{k})}_{LSX}(t))\hat{\rho}^{(\bar{k})}(t)\}, \tag{3.40}$$

where $\hat{H}^{(k)}_{LSX}(t)\approx tr_{\bar{k}}\{(\hat{H}_{int}-\hat{H}^{(\bar{k})}_{LSX}(t))\hat{\rho}^{(\bar{k})}(t)\}$, and $\langle\varphi_\eta^{(\bar{k})}(t)|\hat{X}|\varphi_\eta^{(\bar{k})}(t)\rangle=tr_{\bar{k}}\{\hat{X}\hat{\rho}^{(\bar{k})}(t)\}$ for any operator $\hat{X}$. Note that these approximative equations are still symmetrical for both subsystems, nevertheless, it is easier to see how asymmetrical physical systems might lead to distinct effective behaviours. For instance, if subsystem (2) is sufficiently large to be regarded as a macroscopic system, it is expected that both the interaction and subsystem (1) dynamics would have a negligible effect on (2), in such a way that $tr_1\{(\hat{H}_{int}-\hat{H}^{(1)}_{LSX}(t))\hat{\rho}^{(1)}(t)\}\approx\hat{H}^{(2)}_{LSX}(t)\approx 0$, and its local effective Hamiltonian is indistinguishable from the bare one:

$$\tilde{H}^{(2)}(t)\approx\hat{H}^{(2)}. \tag{3.41}$$

This, however, still not true for the subsystem (1), since

$$\tilde{H}^{(1)}(t)\approx\hat{H}^{(1)}+tr_2\{\hat{H}_{int}\hat{\rho}^{(2)}(t)\}, \tag{3.42}$$

i.e., its local effective Hamiltonian is determined by the macroscopic state of (2) and the interaction term. In particular, if the former is somehow controllable by a set of time-dependent parameters $\{\boldsymbol{R}_t\}$, such that $\hat{\rho}^{(2)}(t) = \hat{\rho}^{(2)}(\boldsymbol{R}_t)$, we obtain an approximative description of a quantum system whose dynamics is driven by an external semi-classical agent, where

$$i\hbar\frac{d}{dt}\hat{\rho}^{(1)}(t) \approx [\tilde{H}^{(1)}(\boldsymbol{R}_t), \hat{\rho}^{(1)}(t)] \tag{3.43}$$

and

$$\tilde{H}^{(1)}(\boldsymbol{R}_t) \approx \hat{H}^{(1)} + tr_2\{\hat{H}_{int}\hat{\rho}^{(2)}(\boldsymbol{R}_t)\}. \tag{3.44}$$

Hence, as expected, from a fully autonomous quantum description one might obtain an - approximative - asymmetric effective behaviour, under the right conditions. This is exactly the case of a single spin weakly interacting with a magnetic field, for instance, whose controllable parameter is the field intensity. In such cases, the full quantization is possible and desirable, yet, this description level corresponds to a highly complex task for many realistic scenarios, and the expressions above correspond to valid approximative characterization of the local dynamics. Nevertheless, from a quantum thermodynamic point of view, it is important to highlight that outside this specific scope the neglected energetic contributions will result in incomplete thermodynamic descriptions.

3.4 Internal energy and additivity

As mentioned earlier, there is no ambiguity in identifying the internal energy of isolated quantum systems: this role is naturally assigned to the expectation value of the Hamiltonian generating its dynamics. However, it is not entirely clear how to obtain a consistent and meaningful analogous to arbitrary open quantum systems. In such cases, the notion of local internal energy is blurred by non-negligible interactions and correlations that might exist within the whole. Thus, any general and coherent definition should somehow account for these elements. Additionally, it is important to emphasize that a clear understanding of internal energy is the most obvious first step toward proper definitions of other fundamental thermodynamic quantities in the quantum regime, especially quantum heat and work. In this section, we argue that the local effective Hamiltonians are the representative physical operators for characterizing the subsystems internal energies. Furthermore, given this identification, we show that the thermodynamic notion of energy additivity is naturally recovered.

3.4.1 The whole and the parts internal energies

By hypothesis, the whole system is closed and autonomous, which means that no energy flows inward or outward. Thus, we immediately identify the total internal energy $U^{(0)}$ as the expectation value of the total Hamiltonian $\hat{H}^{(0)}$, i.e.,

$$U^{(0)} \equiv \langle\hat{H}^{(0)}\rangle = \langle\Psi(t)|\hat{H}^{(0)}|\Psi(t)\rangle, \tag{3.45}$$

where $|\Psi(t)\rangle = \hat{\mathcal{U}}(t,t_0)|\Psi(t_0)\rangle$ and $\hat{\mathcal{U}}(t,t_0) = e^{-\frac{i}{\hbar}\hat{H}^{(0)}(t-t_0)}$. Moreover, it is easy to see that this quantity is indeed conserved[i],

$$\frac{d}{dt}U^{(0)} = 0. \tag{3.46}$$

However, since we are dealing with a bipartite system, from Eq. (3.1) we are able to rewrite $U^{(0)}$ as

$$U^{(0)} = \langle \hat{H}^{(1)}\rangle(t) + \langle \hat{H}^{(2)}\rangle(t) + \langle \hat{H}_{int}\rangle(t) \tag{3.47}$$

where $\langle . \rangle \equiv \langle \Psi(t)|(.)|\Psi(t)\rangle$ and, therefore,

$$\langle \hat{H}^{(k)}\rangle(t) = tr_k\{\hat{H}^{(k)}\hat{\rho}^{(k)}(t)\} = \sum_{j=1}^{d^{(1)}} \lambda_j^2(t)\langle \varphi_j^{(k)}(t)|\hat{H}^{(k)}|\varphi_j^{(k)}(t)\rangle. \tag{3.48}$$

Notice that the total internal energy is the sum of the expectation values of the bare Hamiltonians plus the interaction between the subsystems. It is worth mentioning that, even though these operators are constant, the time-dependency of their expectation values is due to the state dynamics, in such a way that any change in $\langle \hat{H}^{(1)}\rangle(t) + \langle \hat{H}^{(2)}\rangle(t)$ induces the negative variation in $\langle \hat{H}_{int}\rangle(t)$, i.e.,

$$\frac{d}{dt}\langle \hat{H}^{(1)}\rangle(t) + \frac{d}{dt}\langle \hat{H}^{(2)}\rangle(t) = -\frac{d}{dt}\langle \hat{H}_{int}\rangle(t). \tag{3.49}$$

From the previous equations, it is not clear how to properly assign internal energies for each subsystem. Given that the interaction term actively influences their local dynamics, it is reasonable to assume that its contribution should be somehow shared between them. Besides, it is also desirable two relevant properties for the local energies: **(i)** be obtained by local measurements, i.e., associated with the expectation value of local operators; **(ii)** be an additive quantity (extensive property). While the first condition guarantees a local description and accessibility, the second also allows the intuitive picture of energy flowing from one system to another without including energetic sinks or sources, i.e., the sum of the local internal energies is a conserved quantity. These features, of course, are not trivial, especially because the interaction term acts on the whole Hilbert space, which means that it is a global property per se. This fact, however, suggests that an effective approach for describing local internal energy provides the most promising route. Otherwise, a global picture would be necessary for fully characterizing the energetic flux, which is impractical for most realistic scenarios.

Different approaches for how accounting the interaction input can be found in the literature. (156, 162, 164, 188–190) Nevertheless, the most common route in quantum thermodynamics is to directly identify local internal energies as the expectation values of the bare Hamiltonians. Consequently, the sum of the parts is not equal to the whole, and

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[i] The unitary evolution and constant Hamiltonian guarantee the following equality for all t: $\langle \Psi(t)|\hat{H}^{(0)}|\Psi(t)\rangle = \langle \Psi(t_0)|\hat{H}^{(0)}|\Psi(t_0)\rangle$.

the total internal energy is not additive, in general (in contrast with classical scenarios). To circumvent this issue, it is also usually necessary to assume additional hypotheses[j] on the form and/or strength of the interaction operator. After all, if the interaction could be ignored the recognition of local internal energies would be immediate, and the two desired properties would be automatically satisfied. In this sense, the so-called weak-coupling approximation is the most frequent assumption when dealing with open quantum systems dynamics. It explicitly assumes that the interaction term is small enough to be treated as a perturbation. The formal procedure follows the usual perturbative recipe: which consists in scaling the interaction term, such that $\hat{H}_{int} \to \alpha \hat{H}_{int}$, then expanding the local states in a series of α and, finally, discarding high order terms, i.e.,

$$\hat{\rho}^{(k)}(t) = e^{\frac{i}{\hbar}\hat{H}^{(k)}(t-t_0)}\hat{\rho}^{(k)}(t_0)e^{-\frac{i}{\hbar}\hat{H}^{(k)}(t-t_0)} + \alpha\hat{\rho}_1^{(k)}(t) + \alpha^2\hat{\rho}_2^{(k)}(t) + \mathcal{O}(\alpha^3), \tag{3.50}$$

where $\hat{\rho}_n^{(k)}(t)$ is the n-th order correction. In such expansion, the zeroth-order component is simply the initial state time-evolved under the local bare Hamiltonian. Thus non-trivial behaviour is only achieved if considered at least first-order contributions, especially for obtaining non-unitary dynamics. This reasoning alone, nevertheless, is not enough to justify the previous local internal energy identification, given that the interaction term itself is also in the first order and, consequently, it is still relevant in the energetic balance, i.e., $U^{(0)} = \langle \hat{H}^{(1)} \rangle(t) + \langle \hat{H}^{(2)} \rangle(t) + \alpha \langle \hat{H}_{int} \rangle(t)$. Interestingly, in the classical macroscopic thermodynamic setting - *a priori* - we would also have $U^{(0)} = U^{(1)} + U^{(2)} + U_{int}$, however, the interaction input is several orders of magnitude smaller than the other two individual elements, which supports its prompt negligence[k]. It is worth mentioning that the usual derivation of master equations in the Lindblad-like form is based on the second-order expansions and also relies on other restrictive approximations, like Markov and secular ones. (40) Still, even in such cases, there is no reason for not considering the interaction. As an alternative, another common approach is to assign the role of local internal energy for the operator arising in the unitary part of the dynamical equation, which may automatically contain the local bare Hamiltonian plus a correction due to the interaction. (191) In this context, the generator usually has the following superoperator structure $\hat{\mathfrak{L}}_t = \hat{\mathfrak{H}}_t + \hat{\mathfrak{D}}_t$, where $\mathfrak{H}_t \hat{\rho}^{(k)}(t) = [\hat{h}(t), \hat{\rho}^{(k)}(t)]$ is the desired unitary element and $\hat{\mathfrak{D}}_t$ is the dissipator. Such procedure, however, should be carefully considered since $\hat{\mathfrak{H}}_t$ may change over transformations that keep the generator invariant. Thus complementary hypothesis may be required for unambiguously fixing $\hat{h}(t)$. For a recent proposal, see. (164)

Instead of focusing on the interaction strength, one might assume specific Hamiltonian structures. For instance, given the expectation value $\langle \hat{H}_{int} \rangle(t) = \langle \Psi(t) | \hat{H}_{int} | \Psi(t) \rangle$

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[j] Although sometimes not explicitly.

[k] In the paradigmatic example of two ideal gases separated by a partition, the interaction is intermediated by the former, and its energy is proportional to its surface. This energy, however, is negligible compared with the ones stored in each gas.

it is easy to see that its time-evolution obeys the following equation

$$i\hbar\frac{d}{dt}\langle\hat{H}_{int}\rangle(t) = \langle[\hat{H}_{int},(\hat{H}^{(1)}\otimes\hat{1}^{(2)}+\hat{1}^{(1)}\otimes\hat{H}^{(2)})]\rangle. \tag{3.51}$$

The *strict energy conservation* (SEC) condition is the assumption that the commutator above is null, i.e., $[\hat{H}_{int},(\hat{H}^{(1)}\otimes\hat{1}^{(2)}+\hat{1}^{(1)}\otimes\hat{H}^{(2)})]=0$ (150), which leads to a constant expectation value of $\langle\hat{H}_{int}\rangle(t)=cte$ and, therefore,

$$SEC: \qquad \frac{d}{dt}\langle\hat{H}^{(1)}\rangle(t) = -\frac{d}{dt}\langle\hat{H}^{(2)}\rangle(t). \tag{3.52}$$

Hence, if we accept the bare Hamiltonians as the representative operators, despite the local internal energies still not being additive, the energy flowing from one subsystem is necessarily obtained by the other, i.e., the interaction neither captures nor releases any additional energy. This fact justifies neglecting the interaction term into the dynamical energetic analysis within this quantum system. Besides, the SEC condition also implies that $\hat{\mathcal{U}}(t,t_0)$ is a so-called *energy-preserving unitary* (EPU)[1], i.e.,

$$SEC \Rightarrow [\hat{\mathcal{U}}(t,t_0),(\hat{H}^{(1)}\otimes\hat{1}^{(2)}+\hat{1}^{(1)}\otimes\hat{H}^{(2)})]=0, \tag{3.53}$$

which constitute a free operation in the context of resource theory of thermal operations (192). Even though both SEC and EPU represents useful scenarios, they also serve as very restrictive conditions in the form of $\hat{H}_{int}$.

Despite its versatility and relevance, it is clear that approximative procedures and particular hypotheses are only suitable for especific regimes, and a general approach is necessary for developing a fully quantum thermodynamic description of arbitrary systems.

3.4.1.1 Local effective internal energy

In Section (3.2), we obtained the local effective Hamiltonian $\tilde{H}^{(k)}(t)$ as the generator of the local Schmidt basis dynamics of subsystem (k) (Eq. (3.13)), and showed that it can be directly related to the bare Hamiltonian through Eq. (3.18). In Section (3.3), we also showed that the unitary part of the local state dynamics $i\hbar\frac{d}{dt}\hat{\rho}^{(k)}(t)$ is parametrized by $\tilde{H}^{(k)}(t)$. Let us now argue that such Hamiltonians can be seen as the representative local operators for characterizing the physical internal energy.

First, by definition, both $\tilde{H}^{(1)}(t)$ and $\tilde{H}^{(2)}(t)$ are local objects, which means that they can be accessible by local measurements, such that their expectation values are simply $\langle\tilde{H}^{(k)}(t)\rangle = \langle\Psi(t)|\tilde{H}^{(k)}(t)|\Psi(t)\rangle = tr_k\{\tilde{H}^{(k)}(t)\hat{\rho}^{(k)}(t)\}$. Now, we are interested to investigate their relationship with the whole internal energy $U^{(0)}$. Given Eq. (3.3) and

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[1] It also implies that simultaneous local Gibbs states are fixed points of the dynamics, since $\hat{\mathcal{U}}(t,t_0)(e^{-\beta\hat{H}^{(1)}}\otimes e^{-\beta\hat{H}^{(2)}})\hat{\mathcal{U}}^{\dagger}(t,t_0)=e^{-\beta\hat{H}^{(1)}}\otimes e^{-\beta\hat{H}^{(2)}}$. In fact, any state that is a function of its bare Hamiltonian would be.

Eq. (3.13) for the Schmidt decomposition and the Schmidt basis dynamics, we have the following equation

$$i\hbar\frac{d}{dt}|\Psi(t)\rangle = \sum_{j=1}^{d^{(1)}}\left(i\hbar\frac{d}{dt}\lambda_j(t)\right)|\varphi_j^{(1)}(t)\rangle\otimes|\varphi_j^{(2)}(t)\rangle + \left(\tilde{H}^{(1)}(t)+\tilde{H}^{(2)}(t)\right)|\Psi(t)\rangle. \tag{3.54}$$

Thus, since $i\hbar\frac{d}{dt}|\Psi(t)\rangle = \hat{H}^{(0)}|\Psi(t)\rangle$, it is easy to see that

$$\begin{aligned}\langle\Psi(t)|\hat{H}^{(0)}|\Psi(t)\rangle = \langle\Psi(t)|\sum_{j=1}^{d^{(1)}}\left(i\hbar\frac{d}{dt}\lambda_j(t)\right)|\varphi_j^{(1)}(t)\rangle\otimes|\varphi_j^{(2)}(t)\rangle \\ + \langle\Psi(t)|\tilde{H}^{(1)}(t)|\Psi(t)\rangle + \langle\Psi(t)|\tilde{H}^{(2)}(t)|\Psi(t)\rangle.\end{aligned} \tag{3.55}$$

However, notice that due to normalization of $|\Psi(t)\rangle$, the first contribution is necessarily null,

$$\langle\Psi(t)|\sum_{j=1}^{d^{(1)}}\left(i\hbar\frac{d}{dt}\lambda_j(t)\right)|\varphi_j^{(1)}(t)\rangle\otimes|\varphi_j^{(2)}(t)\rangle = i\hbar\sum_{j=1}^{d^{(1)}}\lambda_j(t)\frac{d}{dt}\lambda_j(t) = 0, \tag{3.56}$$

since $\sum_{j=1}^{d^{(1)}}\lambda_j^2(t) = 1$, and $\sum_{j=1}^{d^{(1)}}\lambda_j(t)\frac{d}{dt}\lambda_j(t) = \frac{1}{2}\frac{d}{dt}\sum_{j=1}^{d^{(1)}}\lambda_j^2(t)$. Hence, surprisingly, the expectation value of the whole Hamiltonian $\hat{H}^{(0)}$ is exactly equal to the sum of the expectation values of the local effective ones, i.e.,

$$\langle\hat{H}^{(0)}\rangle = \langle\tilde{H}^{(1)}(t)\rangle + \langle\tilde{H}^{(2)}(t)\rangle = U^{(0)}. \tag{3.57}$$

If we identify $\langle\tilde{H}^{(1)}(t)\rangle$ and $\langle\tilde{H}^{(2)}(t)\rangle$ as the physical *local (effective) internal energies* along the respective paths $\{\mathcal{P}_j^{(1)}\}_j$ and $\{\mathcal{P}_j^{(2)}\}_j$, such that

$$U^{(k)}(t) := \langle\tilde{H}^{(k)}(t)\rangle = i\hbar\sum_{j=1}^{d^{(1)}}\lambda_j^2(t)\langle\varphi_j^{(k)}(t)|\frac{d}{dt}|\varphi_j^{(k)}(t)\rangle, \tag{3.58}$$

we automatically account for both the bare and interaction contributions,

$$U^{(k)} = \langle\hat{H}^{(k)}\rangle(t) + \langle\hat{H}_{LS}^{(k)}(t)\rangle + \langle\hat{H}_X^{(k)}(t)\rangle, \tag{3.59}$$

in such a way that we directly guarantee the additivity of energy (extensive property),

$$U^{(0)} = U^{(1)}(t) + U^{(2)}(t), \tag{3.60}$$

and, consequently, that the energy flowing from subsystem (1) is fully captured by subsystem (2) and vice versa, i.e.,

$$\frac{d}{dt}U^{(1)}(t) = -\frac{d}{dt}U^{(2)}(t). \tag{3.61}$$

It is important to emphasize that such equalities are exact, and no additional hypotheses were required[m].

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[m] While in classical thermodynamics energy additivity is an approximative idealization (justified by the negligible interaction), in this context, this is an exact statement.

Furthermore, it was mentioned earlier that, intuitively, both operators $\hat{H}_{LS}^{(k)}(t)$ and $\hat{H}_{X}^{(k)}(t)$ are byproducts of the interaction term. In fact, it is possible to show that their expectation values are directly related. From Eq. (3.47) and Eq.(3.57), we have the following equality

$$\langle \hat{H}^{(1)}\rangle(t) + \langle \hat{H}^{(2)}\rangle(t) + \langle \hat{H}_{int}\rangle(t) = \langle \tilde{H}^{(1)}(t)\rangle + \langle \tilde{H}^{(2)}(t)\rangle, \tag{3.62}$$

and, therefore, since Eq. (3.59),

$$\langle \hat{H}_{int}\rangle(t) = \langle \hat{H}_{LS}^{(1)}(t)\rangle + \langle \hat{H}_{X}^{(1)}(t)\rangle + \langle \hat{H}_{LS}^{(2)}(t)\rangle + \langle \hat{H}_{X}^{(2)}(t)\rangle. \tag{3.63}$$

The previous equation states how the energetic contribution coming from the interaction term is symmetrically shared between the subsystems[n], and how its change affects the local internal energies. Interestingly, notice that the SEC condition, Eq. (3.51), is analogous to supposing that

$$SEC: \qquad \frac{d}{dt}\langle \hat{H}_{LS}^{(1)}(t) + \hat{H}_{X}^{(1)}(t)\rangle = -\frac{d}{dt}\langle \hat{H}_{LS}^{(2)}(t) + \hat{H}_{X}^{(2)}(t)\rangle, \tag{3.64}$$

i.e., the change of the subsystem (1) local internal energy due to $\hat{H}_{LS}^{(1)}(t) + \hat{H}_{X}^{(1)}(t)$ dynamics is perfectly balanced by $\hat{H}_{LS}^{(2)}(t) + \hat{H}_{X}^{(2)}(t)$, in a way that their net change is null.

In summary, the recognition of the local effective Hamiltonians as the representative operators for describing the physical internal energies allow us to consistently refer to these local quantities without explicitly mentioning global properties. Most importantly, this procedure is exact and general and, thus, applicable to *any* setting and regime. We consider this as one of our main results.

3.5 Local phase gauge

It was mentioned earlier that even though the Schmidt coefficients $\{\lambda_j(t)\}_j$ are unambiguously defined by the Schmidt decomposition, its basis $\{|\varphi_j^{(k)}(t)\rangle\}_{j,k}$ are unique up to degeneracy and a phase component. In this section, we will present and investigate how the latter ambiguity influences our local effective description. Then we will discuss and emphasize its consequences at the energetic level and argue how to, possibly, fix such a freedom.

Generally speaking, phases are intrinsic to the mathematical formalism of quantum mechanics. In fact, it is a direct consequence of representing physical quantum states in Hilbert spaces. It is often common to introduce the concept of global and relative phases. While the former is usually treated as simply artefacts, the latter are viewed as sources of fundamentally quantum behaviour, e.g., coherence. However, it is worth mentioning that despite being superfluous for any physical description and measurement, global phases

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[n] Of course, this does not imply that their modulus cannot be extremely different.

are deeply connected with the underlying geometry of these abstract structures and far from being unimportant[o]. More specifically, given a Hilbert space $\mathcal{H}$, physical states are not uniquely related to kets from $\mathcal{H}$, i.e., both $|\Psi\rangle \in \mathcal{H}$ and $|\Psi'\rangle = e^{i\theta}|\Psi\rangle \in \mathcal{H}$, simply differing by $e^{i\theta}$, represents the same physical system for any θ real. Given the measurement postulate, note that all possible extractable information from $|\Psi\rangle$ is also equally encoded by $|\Psi'\rangle$. Such phases invariance illustrates a fundamental gauge transformation inbuilt in the core of the theory. That said, let us now consider an arbitrary Schmidt decomposition, presented by Eq. (2.53). It is clear that the simultaneous addition of local phases $\{\theta_\eta\}_\eta$, such that

$$|\varphi_\eta^{(1)}\rangle \to |\varphi_\eta'^{(1)}\rangle = e^{i\theta_\eta}|\varphi_\eta^{(1)}\rangle, \tag{3.65}$$

$$|\varphi_\eta^{(2)}\rangle \to |\varphi_\eta'^{(2)}\rangle = e^{-i\theta_\eta}|\varphi_\eta^{(2)}\rangle, \tag{3.66}$$

maintains the whole quantum state structure unchanged since the phases cancel out and, therefore,

$$|\Psi\rangle = \sum_{\eta=1}^{n} \lambda_\eta |\varphi_\eta^{(1)}\rangle \otimes |\varphi_\eta^{(2)}\rangle = \sum_{\eta=1}^{n} \lambda_\eta |\varphi_\eta'^{(1)}\rangle \otimes |\varphi_\eta'^{(2)}\rangle = |\Psi'\rangle. \tag{3.67}$$

Interestingly, from a local point of view, any phase gauge transformation is valid in the sense that it keeps describing the same physical state. Nevertheless, from a global perspective, the same phases (in modulus) should be included in the remaining Schmidt basis to guarantee consistency. Otherwise, we would be adding relative phases and changing the whole system state $|\Psi\rangle$. Such "flexibility" corresponds to an internal freedom within the Schmidt decomposition itself[p] that, naturally, will be inherited by our description. Along these lines, considering the set of simultaneous coupled trajectories $\mathcal{P}_j^{(1,2)}$ followed by the Schmidt basis $|\varphi_j^{(1,2)}(t)\rangle$ in $\mathcal{H}^{(1,2)}$, we might define a set of real functions $\{\theta_j(t)\}_j$ for $t \in [t_0, t_1]$ that transform the curves $\{\mathcal{P}_j^{(1,2)}\}_j$ into a new phase gauge $\{\mathcal{P}_j'^{(1,2)}\}_j$ that still represent the whole state trajectory $\mathcal{P}^{(0)}$ of $|\Psi(t)\rangle$ in the total Hilbert space $\mathcal{H}^{(0)}$, i.e.,

$$\mathcal{P}_j^{(1)} \to \mathcal{P}_j'^{(1)} : |\varphi_j'^{(1)}(t)\rangle = e^{i\theta_j(t)}|\varphi_j^{(1)}(t)\rangle,\ t \in [t_0, t_1], \tag{3.68}$$

$$\mathcal{P}_j^{(2)} \to \mathcal{P}_j'^{(2)} : |\varphi_j'^{(2)}(t)\rangle = e^{-i\theta_j(t)}|\varphi_j^{(2)}(t)\rangle,\ t \in [t_0, t_1], \tag{3.69}$$

such that $\mathcal{P}^{(0)} \to \mathcal{P}'^{(0)} = \mathcal{P}^{(0)}$ and $\langle \varphi_\alpha'^{(k)}(t)|\varphi_\beta'^{(k)}(t)\rangle = e^{(-1)^{k-1} i(\theta_\beta(t)-\theta_\alpha(t))}\delta_{\alpha\beta}$. Of course, given that the physical kets are invariant under such transformations, it is clear that both local density operators $\hat{\rho}^{(1,2)}(t)$ (Eqs. (3.5, 3.6)) and their trajectories $\mathcal{C}^{(1,2)} : \hat{\rho}^{(1,2)}(t)$, $t \in [t_0, t_1]$ along the state space $\mathscr{D}(\mathcal{H}^{(k)})$ are not sensible to phase changes, $\hat{\rho}'^{(1,2)}(t) = \hat{\rho}^{(1,2)}(t)$. Nevertheless, since the local effective Hamiltonians $\tilde{H}^{(1,2)}(t)$, given by Eq. (3.14), are functionals of the Schmidt basis, it is straightforward to see that they intrinsically depend

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[o] The notion of geometric phase, for instance, arises in such context and, since initial developments by Berry (193), it became clear its importance for the complete understanding of quantum mechanics.

[p] More fundamentally, it comes from the singular value decomposition.

on the chosen gauge. If we perform the transformations $\mathcal{P}_j^{(1,2)} \to \mathcal{P}_j^{\prime(1,2)}$ above and use the expression $i\hbar\frac{d}{dt}|\varphi_j^{(k)}(t)\rangle = \tilde{H}^{(k)}(t)|\varphi_j^{(k)}(t)\rangle$ we obtain

$$i\hbar\frac{d}{dt}|\varphi_j^{\prime(1)}(t)\rangle = \left(\tilde{H}^{(1)}(t) - \hbar\frac{d\theta_j(t)}{dt}\right)|\varphi_j^{\prime(1)}(t)\rangle, \tag{3.70}$$

$$i\hbar\frac{d}{dt}|\varphi_j^{\prime(2)}(t)\rangle = \left(\tilde{H}^{(2)}(t) + \hbar\frac{d\theta_j(t)}{dt}\right)|\varphi_j^{\prime(2)}(t)\rangle, \tag{3.71}$$

for the Schmidt basis dynamics. Then, it is clear that the local effective Hamiltonians in the new gauge, $\tilde{H}^{\prime(1,2)}(t)$, might be directly related to those from the old ones, such that

$$\tilde{H}^{\prime(1)}(t) \equiv i\hbar\sum_{j=1}^{d^{(1)}}\frac{d}{dt}|\varphi_j^{\prime(1)}(t)\rangle\langle\varphi_j^{\prime(1)}(t)| = \tilde{H}^{(1)}(t) - \hbar\sum_{j=1}^{d^{(1)}}\left(\frac{d\theta_j(t)}{dt}\right)|\varphi_j^{(1)}(t)\rangle\langle\varphi_j^{(1)}(t)|, \tag{3.72}$$

$$\tilde{H}^{\prime(2)}(t) \equiv i\hbar\sum_{j=1}^{d^{(2)}}\frac{d}{dt}|\varphi_j^{\prime(2)}(t)\rangle\langle\varphi_j^{\prime(2)}(t)| = \tilde{H}^{(2)}(t) + \hbar\sum_{j=1}^{d^{(2)}}\left(\frac{d\theta_j(t)}{dt}\right)|\varphi_j^{(2)}(t)\rangle\langle\varphi_j^{(2)}(t)|. \tag{3.73}$$

Observe that a gauge change adds an extra term, $\hbar\sum_{j=1}^{d^{(1,2)}}\left(\frac{d\theta_j(t)}{dt}\right)|\varphi_j^{(1,2)}(t)\rangle\langle\varphi_j^{(1,2)}(t)|$, that only depends on the time derivative of the phases and are diagonal on their respective Schmidt basis. In general, these additional quantities will change the operator structure in a way that both their eigenbasis and eigenvalues will be affected. This implies that, for most cases, the spectral gaps will not maintain fixed[q] and $[\tilde{H}^{\prime(k)}(t), \tilde{H}^{(k)}(t)] \neq 0$. Besides, the extra term form means that $[\sum_{j=1}^{d^{(1,2)}}\left(\frac{d\theta_j(t)}{dt}\right)|\varphi_j^{(1,2)}(t)\rangle\langle\varphi_j^{(1,2)}(t)|, \hat{\rho}^{(1,2)}(t)] = 0$ for all t, which also guarantees the invariance of the local state dynamics written in Eq. (3.28). Concerning the expectation values of $\tilde{H}^{\prime(1,2)}(t)$, by directly computing $\langle\tilde{H}^{\prime(k)}(t)\rangle = \langle\Psi'(t)|\tilde{H}^{\prime(k)}(t)|\Psi'(t)\rangle$ we see that a phase gauge transformation just perform a shift in the mean value obtained from the previous gauge, i.e.,

$$\langle\tilde{H}^{\prime(1)}(t)\rangle = \langle\tilde{H}^{(1)}(t)\rangle - \hbar\sum_{j=1}^{d^{(1)}}\lambda_j^2(t)\left(\frac{d\theta_j(t)}{dt}\right), \tag{3.74}$$

$$\langle\tilde{H}^{\prime(2)}(t)\rangle = \langle\tilde{H}^{(2)}(t)\rangle + \hbar\sum_{j=1}^{d^{(1)}}\lambda_j^2(t)\left(\frac{d\theta_j(t)}{dt}\right). \tag{3.75}$$

Interestingly, the shift accumulated by subsystem (1), $\hbar\sum_{j=1}^{d^{(1)}}\lambda_j^2(t)\left(\frac{d\theta_j(t)}{dt}\right)$, is compensated by the one acquired by subsystem (2)[r]. Hence, as expected, such a phase gauge automatically ensures that the additivity property obtained in Eq. (3.57) is still satisfied for any transformation:

$$U^{(0)} = \langle\hat{H}^{(0)}\rangle = \langle\tilde{H}^{(1)}(t)\rangle + \langle\tilde{H}^{(2)}(t)\rangle = \langle\tilde{H}^{\prime(1)}(t)\rangle + \langle\tilde{H}^{\prime(2)}(t)\rangle, \tag{3.76}$$

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[q] If $\{\epsilon_j^{(k)}(t)\}_j$ and $\{\epsilon_j^{\prime(k)}(t)\}_j$ are the eigenvalues of $\tilde{H}^{(k)}(t)$ and $\tilde{H}^{\prime(k)}(t)$, respectively. Then, the gaps are simply defined by the changes $\hbar\omega_{\alpha\beta}^{(k)}(t) = \epsilon_\beta^{(k)}(t) - \epsilon_\alpha^{(k)}(t)$. And, in general, for two different gauges, we have $\hbar\omega_{\alpha\beta}^{\prime(k)}(t) = \epsilon_\beta^{\prime(k)}(t) - \epsilon_\alpha^{\prime(k)}(t) \neq \epsilon_\beta^{(k)}(t) - \epsilon_\alpha^{(k)}(t) = \hbar\omega_{\alpha\beta}^{(k)}(t)$.

[r] Since there are only $d^{(1)}$ Schmidt coefficients, we have $\lambda_\eta(t) = 0$ for $d^{(1)} < \eta \leq d^{(2)}$, and the following equality $\sum_{j=1}^{d^{(2)}}\lambda_j^2(t)\left(\frac{d\theta_j(t)}{dt}\right) = \sum_{j=1}^{d^{(1)}}\lambda_j^2(t)\left(\frac{d\theta_j(t)}{dt}\right)$ is satisfied.

and, therefore,

$$\frac{d}{dt}\langle \tilde{H}'^{(1)}(t)\rangle = -\frac{d}{dt}\langle \tilde{H}'^{(2)}(t)\rangle. \tag{3.77}$$

Finally, it is clear that for every phase gauge, there is a pair of local effective Hamiltonians $\tilde{H}'^{(1,2)}(t)$ attained to it. However, this poses a fundamental obstacle for interpreting their expectation values as the *physical* local effective internal energies: after all, if all gauges correspond to the same physical state, which one is the representative one for characterizing the internal energies?

Of course, different choices may lead to very distinct conclusions. Yet, not all possibilities preserve some of the desired properties. For instance, since any set $\{\theta_j(t)\}_j$ represents a valid gauge (as long as it is a real function), let us strategically choose

$$\hbar\frac{d}{dt}\theta_j(t) = \langle \varphi_j^{(1)}(t)|\tilde{H}^{(1)}(t)|\varphi_j^{(1)}(t)\rangle, \tag{3.78}$$

for all j. Thus, Eq. (3.72) becomes

$$\tilde{H}'^{(1)}(t) = \tilde{H}^{(1)}(t) - \sum_{j=1}^{d^{(1)}}\langle \varphi_j^{(1)}(t)|\tilde{H}^{(1)}(t)|\varphi_j^{(1)}(t)\rangle|\varphi_j^{(1)}(t)\rangle\langle\varphi_j^{(1)}(t)|, \tag{3.79}$$

which, essentially, subtracts from $\tilde{H}^{(1)}(t)$ its diagonal elements in the instantaneous Schmidt basis representation, $\langle \varphi_j^{(1)}(t)|\tilde{H}^{(1)}(t)|\varphi_j^{(1)}(t)\rangle$. Also, notice it implies the mean value from Eq. (3.74) is null for all t,

$$\langle \tilde{H}'^{(1)}(t)\rangle = 0 \tag{3.80}$$

since $\hbar\sum_{j=1}^{d^{(1)}}\lambda_j^2(t)\left(\frac{d\theta_j(t)}{dt}\right) = \langle \tilde{H}^{(1)}(t)\rangle$. Nevertheless, this difference is compensated by subsystem (2), such that

$$\langle \tilde{H}'^{(2)}(t)\rangle = \langle \tilde{H}^{(2)}(t)\rangle + \langle \tilde{H}^{(1)}(t)\rangle, \tag{3.81}$$

and $U^{(0)} = \langle \tilde{H}'^{(2)}(t)\rangle = \langle \tilde{H}^{(1)}(t)\rangle + \langle \tilde{H}^{(2)}(t)\rangle$ remains invariant. As we can see, according to this phase gauge choice, if we identify $U^{(k)}(t) := \langle \tilde{H}'^{(k)}(t)\rangle$, there is no energetic flow since $\frac{d}{dt}\langle \tilde{H}'^{(1,2)}(t)\rangle = 0$, and all the internal energy of the whole bipartite system is gathered exclusively by the subsystem (2), which eliminates our symmetrical perspective. Moreover, the opposite conclusion is obtained if considered $\hbar\frac{d}{dt}\theta_j(t) = -\langle \varphi_j^{(2)}(t)|\tilde{H}^{(2)}(t)|\varphi_j^{(2)}(t)\rangle$ instead. Interestingly, given Eq. (3.72), the assumption from Eq. (3.78) translates to $\langle \varphi_j'^{(1)}(t)|\frac{d}{dt}|\varphi_j'^{(1)}(t)\rangle = 0$ for all j, i.e., we are dealing with the gauge where all kets $\{|\varphi_j'^{(1)}(t)\rangle\}_j$ are parallel transported. (194)

Alternatively, we may also assume the following gauge

$$\hbar\frac{d\theta_j(t)}{dt} = \langle \varphi_j^{(1)}(t)|\hat{H}_{LS}^{(1)}(t)|\varphi_j^{(1)}(t)\rangle + \langle \varphi_j^{(1)}(t)|\hat{H}_{X}^{(1)}(t)|\varphi_j^{(1)}(t)\rangle. \tag{3.82}$$

In this case, we have $\langle \varphi_j'^{(1)}(t)|\tilde{H}'^{(1)}(t)|\varphi_j'^{(1)}(t)\rangle = \langle \varphi_j^{(1)}(t)|\hat{H}^{(1)}|\varphi_j^{(1)}(t)\rangle$ for all j and, therefore,

$$\hbar\sum_{j=1}^{d^{(1)}}\lambda_j^2(t)\left(\frac{d\theta_j(t)}{dt}\right) = \langle \hat{H}_{LS}^{(1)}(t)\rangle + \langle \hat{H}_{X}^{(1)}(t)\rangle, \tag{3.83}$$

which also implies that all energetic contributions for subsystem (1) except coming from its bare Hamiltonian are eliminated, such that

$$\langle \tilde{H}'^{(1)}(t)\rangle = \langle \hat{H}^{(1)}\rangle(t), \tag{3.84}$$

and, consequently, $\langle \tilde{H}'^{(2)}(t)\rangle = \langle \tilde{H}^{(2)}(t)\rangle + \langle \hat{H}^{(1)}_{LS}(t)\rangle + \langle \hat{H}^{(1)}_{X}(t)\rangle$. However, given Eq. (3.63), we obtain that

$$\langle \tilde{H}'^{(2)}(t)\rangle = \langle \hat{H}^{(2)}\rangle(t) + \langle \hat{H}_{int}\rangle(t), \tag{3.85}$$

i.e., if we identify $U^{(k)}(t) := \langle \tilde{H}'^{(k)}(t)\rangle$, it would be concluded that the local internal energy of subsystem (1) is fully characterized by its bare Hamiltonian, $\hat{H}^{(1)}$, and all the interaction contributions belong entirely to subsystem (2). Again, this perspective also breaks our desired symmetrical description, and, clearly, by correctly changing the gauge, the opposite roles can be easily obtained. Moreover, it is interesting to notice that, essentially, this gauge corresponds to the usual identification of the local internal energies.

3.5.1 Frame change

Before attempting to answer the earlier questioning, let us now recast the previous discussion in the language of frame changes. In general, frame changes are represented by unitary operators $\hat{\Theta}(t)$ that map - in a convenient way - a given physical state from one representation to another, i.e., $|\psi\rangle \to |\psi'\rangle = \hat{\Theta}(t)|\psi\rangle$[s]. Such unitaries keep observation outcomes from different frames invariant, i.e., the observables also change in a way that maintains their spectra unaffected. This behaviour, however, is not observed for the whole Hamiltonian in particular, since the Schrödinger equation must be covariant under these frame transformations. This result is analogous to changing the frame of reference and, consequently, the potential energy in classical mechanics: the internal energy computed by different external observers will depend on their particular frames, and despite observing distinct dynamics on their subjective perspective, they will agree with the mean values. Additionally, this also implies there is no fundamental privileged frame since all possibilities are equally valid for describing the system of interest. Thus, by defining the following phase operators

$$\hat{\Theta}^{(1)}(t) = \sum_{j=1}^{d^{(1)}} e^{i\theta_j(t)} |\varphi^{(1)}_j(t)\rangle\langle\varphi^{(1)}_j(t)|, \tag{3.86}$$

$$\hat{\Theta}^{(2)}(t) = \sum_{j=1}^{d^{(2)}} e^{-i\theta_j(t)} |\varphi^{(2)}_j(t)\rangle\langle\varphi^{(2)}_j(t)|, \tag{3.87}$$

and

$$\hat{\Theta}^{(0)}(t) = \hat{\Theta}^{(1)}(t) \otimes \hat{\Theta}^{(2)}(t), \tag{3.88}$$

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[s] Essentially, the well known Heisenberg and interaction pictures are specific cases of these kinds of transformations. The usual "rotating frame" is also an example.

such that $\hat{\Theta}^{(k)}(t)\hat{\Theta}^{(k)\dagger}(t) = \hat{1}^{(k)}$ for $k \in [0,2]$, we can write the whole state transformation as

$$|\Psi'(t)\rangle = \sum_{j=1}^{d^{(1)}} \lambda_j(t)|\varphi_j'^{(1)}(t)\rangle \otimes |\varphi_j'^{(2)}(t)\rangle = \hat{\Theta}^{(0)}(t)|\Psi(t)\rangle, \tag{3.89}$$

while the Schmidt basis phase gauge transformation that are shown in Eqs. (3.68, 3.69) become

$$|\varphi_j'^{(1)}(t)\rangle = \hat{\Theta}^{(1)}(t)|\varphi_j^{(1)}(t)\rangle, \tag{3.90}$$

$$|\varphi_j'^{(2)}(t)\rangle = \hat{\Theta}^{(2)}(t)|\varphi_j^{(2)}(t)\rangle. \tag{3.91}$$

Thus, given the basis time-evolution in the old frame $|\varphi_j^{(k)}(t)\rangle = \tilde{\mathcal{U}}^{(k)}(t,t_0)|\varphi_j^{(k)}(t_0)\rangle$, the time evolution operator in the new frame is simply

$$|\varphi_j'^{(k)}(t)\rangle = \hat{\Theta}^{(k)}(t)\tilde{\mathcal{U}}^{(k)}(t,t_0)\hat{\Theta}^{(k)\dagger}(t_0)|\varphi_j'^{(k)}(t_0)\rangle, \tag{3.92}$$

where $\tilde{\mathcal{U}}'^{(k)}(t,t_0) = \hat{\Theta}^{(k)}(t)\tilde{\mathcal{U}}^{(k)}(t,t_0)\hat{\Theta}^{(k)\dagger}(t_0)$ and the inverse transformation $|\varphi_j^{(k)}(t_0)\rangle = \hat{\Theta}^{(k)\dagger}(t_0)|\varphi_j'^{(k)}(t_0)\rangle$ is automatically guaranteed by the unitarity of the frame change operator. Besides, given the Schrödinger equation $i\hbar\frac{d}{dt}|\Psi(t)\rangle = \hat{H}^{(0)}|\Psi(t)\rangle$ and the basis dynamical equations Eq. (3.13), it is straightforward to show that their forms are covariant over these frame transformations, in a way that

$$i\hbar\frac{d}{dt}|\Psi'(t)\rangle = \hat{H}'^{(0)}(t)|\Psi'(t)\rangle \tag{3.93}$$

and

$$i\hbar\frac{d}{dt}|\varphi_j'^{(k)}(t)\rangle = \tilde{H}'^{(k)}(t)|\varphi_j'^{(k)}(t)\rangle, \tag{3.94}$$

where

$$\hat{H}'^{(0)}(t) \equiv \hat{\Theta}^{(0)}(t)\hat{H}^{(0)}\hat{\Theta}^{(0)\dagger}(t) + i\hbar\left(\frac{d}{dt}\hat{\Theta}^{(0)}(t)\right)\hat{\Theta}^{(0)\dagger}(t), \tag{3.95}$$

$$\tilde{H}'^{(1,2)}(t) \equiv \hat{\Theta}^{(1,2)}(t)\tilde{H}^{(1,2)}(t)\hat{\Theta}^{(1,2)\dagger}(t) + i\hbar\left(\frac{d}{dt}\hat{\Theta}^{(1,2)}(t)\right)\hat{\Theta}^{(1,2)\dagger}(t) \tag{3.96}$$

are the global and local effective Hamiltonians represented in the new frame, respectively. Interestingly, notice that the - once time-independent - global Hamiltonian explicitly depends on time in the transformed frame, in a way that $\langle\Psi'(t)|\left(\frac{d}{dt}\hat{\Theta}^{(0)}(t)\right)\hat{\Theta}^{(0)\dagger}(t)|\Psi'(t)\rangle = 0$ and, therefore,

$$\langle\hat{H}'^{(0)}(t)\rangle = \langle\hat{H}^{(0)}\rangle = U^{(0)}, \tag{3.97}$$

i.e., despite $\hat{H}'^{(0)}(t)$ being time-dependent, its mean value is constant and the conservation of the whole internal energy is still satisfied, as expected. Furthermore, for the mean values of the local effective Hamiltonians in the new frame we have

$$\langle\tilde{H}'^{(1,2)}(t)\rangle = \langle\tilde{H}^{(1,2)}(t)\rangle + i\hbar\left\langle\left(\frac{d}{dt}\hat{\Theta}^{(1,2)}(t)\right)\hat{\Theta}^{(1,2)\dagger}(t)\right\rangle. \tag{3.98}$$

It is easy to check that the frame change expressions above, Eqs. (3.96, 3.98), are the same as the ones presented previously in Eqs. (3.72, 3.73, 3.74, 3.75)[t].

Thus, the internal phase gauge freedom corresponds to a family of frames that consistently describe the whole and the local dynamics. In a way that each possible frame characterizes different Schmidt basis dynamics and, therefore, distinct local effective Hamiltonians, i.e., they are not frame-invariant. Nevertheless, this set of allowed frame transformations guarantees that the whole internal energy remains the same. Hence, the question previously posed becomes: which frame (or frames) is (are) the relevant ones for characterizing the local internal energies?

3.5.2 Recap and gauge fixing proposal

In retrospect, during Section (3.4.1.1), we argued that the local effective Hamiltonians $\tilde{H}^{(1,2)}(t)$ are interesting candidates for being the representative operators for characterizing the physical internal energies in an exact and complete general way. More specifically, it was shown that these operators are hermitian, local - by construction - and also satisfy the usual notion of energy additivity (or extensivity). Then, in the current Section, we just identified that for a unique bipartite physical system there is an intrinsic phase gauge freedom within the Schmidt decomposition structure (see Eq. (3.67)). Such ambiguity translates into a degeneracy for defining those local operators and might be interpreted as the result of the existence of a set of possible frames that consistently describes the subsystems dynamics and the global energetics. In short, for the same physical system and behaviour, we can identify a large family of frames, each one with a particular pair of coupled local effective Hamiltonians $\{\tilde{H}'^{(1)}(t), \tilde{H}'^{(2)}(t)\}$ satisfying $\frac{d}{dt}\langle\tilde{H}'^{(1)}(t)\rangle = -\frac{d}{dt}\langle\tilde{H}'^{(2)}(t)\rangle$, in a way that it is not clear which one should be considered for quantifying the internal energies $U^{(1,2)}(t)$.

Interestingly, this kind of ambiguity is not exclusive to our discussion since it also happens in the classical mechanics context, so let us digress a little bit to the classical realm. In a very general sense, once established the usual Lagrangian formulation of mechanics one may restructure the theory to a Hamiltonian picture simply by performing the following Legendre transformation

$$H(\boldsymbol{q},\boldsymbol{p},t) = \dot{\boldsymbol{q}}.\boldsymbol{p} - L(\boldsymbol{q},\dot{\boldsymbol{q}},t), \tag{3.99}$$

where $\dot{\boldsymbol{q}} = \frac{d\boldsymbol{q}}{dt}$, and $\boldsymbol{q} = \{q_j\}_j^N$ and $\boldsymbol{p} = \{p_j = \frac{\partial L}{\partial \dot{q}_j}\}_j^N$ are the respective N-dimensional set of generalized coordinates and conjugate momenta, while $L(\boldsymbol{q},\dot{\boldsymbol{q}},t)$ and $H(\boldsymbol{q},\boldsymbol{p},t)$ are the

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[t] It is straightforward to see that

$$\langle\Psi'(t)|\left(\frac{d}{dt}\hat{\Theta}^{(k)}(t)\right)\hat{\Theta}^{(k)\dagger}(t)|\Psi'(t)\rangle = (-1)^{k-1} i \sum_{j=1}^{d^{(k)}}\left(\frac{d\theta_j(t)}{dt}\right)\lambda_j^2(t).$$

Lagrangian describing the system and its Hamiltonian, respectively. Thus, to obtain the Hamiltonian of a given problem, it is just required to follow a specific set of mathematical steps. Although straightforward, at least in theory, this might be a very complex procedure. Interestingly, for particular circumstances, there is a formal and justifiable shortcut to this recipe: if the generalized coordinates $\boldsymbol{q}$ do not explicitly depend on time and there are only conservative potentials, the Hamiltonian is necessarily equal to the system's total energy U, i.e.,

$$H = K + V = U, \tag{3.100}$$

where K and V are the kinetic and potential energies, respectively. Therefore, if one of these conditions is unfulfilled the Hamiltonian is not automatically equal to the internal energy. This, nevertheless, represents the most generic situation, with Eq. (3.100) being the particular case. Also, in contrast to the Lagrangian, it is clear that the Hamiltonian description is intrinsically bound to the generalized coordinates, i.e., $L(\boldsymbol{q}, \dot{\boldsymbol{q}}, t)$ may functionally depend on this choice but its numerical value (magnitude) maintains fixed for generalized coordinate changes, while, as emphasized by H. Goldstein in (195), "*the Hamiltonian is dependent both in magnitude and in functional form upon the initial choice of generalized coordinates*". Hence, for the same physical system, one may construct distinct Hamiltonians by employing different sets of generalized coordinates in the definition presented by Eq. (3.99). In particular, a conserved Hamiltonian described by one set of coordinates might be time-dependent in another, which illustrates the fact that the conditions required for the Hamiltonian be the total energy are not the same for being a conserved quantity. For a detailed discussion and examples on these matters, see Chapter 8 of. (195)

So, from the discussion above, it is now clear that the relationship between Hamiltonian and total energy is not always straightforward, even in classical mechanics. In such a context, the existence of different possible generalized coordinates for representing a given system produces an ambiguity that might generate Hamiltonians of different forms, time-dependency and magnitude. Of course, despite not being necessarily equal to the system's total energy, any choice is suitable for consistently describing the dynamics. That said, this situation is analogous to what we obtained before: in both cases, there is a set of valid Hamiltonians and a source of ambiguity, where the frames/phase gauge plays a similar role played by the classical coordinates. However, in the classical scenario, the identification of the Hamiltonian that correctly describes the internal energy is easily checked, i.e., Eq. (3.100) provides an independent prescription for calculating this quantity and comparing the results. Interestingly, even though there is no comparable straightforward manner to inspecting the relationship between the local effective Hamiltonians and energy, we can still identify the set of physically consistent phases and fix the relevant gauges.

First, let us emphasize that the addition of local phases is a consequence of the mathematical freedom within the Schmidt decomposition and does not depend on the Hamiltonian structure of the whole system, i.e., the phases are arbitrary and are independent of the local bare Hamiltonians $\hat{H}^{(1,2)}$ and, more importantly, of the interaction term $\hat{H}_{int}$. Then, as shown earlier in Section (3.2), given the following form for the local effective Hamiltonian $\tilde{H}^{(k)}(t) = \hat{H}^{(k)} + \hat{H}^{(k)}_{LS}(t) + \hat{H}^{(k)}_{X}(t)$, it is clear that the additional terms $\hat{H}^{(k)}_{LS}(t)$ and $\hat{H}^{(k)}_{X}(t)$ are by-products of the existing interaction between the subsystems, i.e., in the absence of $\hat{H}_{int}$ both subsystems would behave independently as isolated objects and their local effective Hamiltonians would be simply identified as their bare ones, $\tilde{H}^{(k)}(t) = \hat{H}^{(k)}$. Note that a similar conclusion should be true *regardless* of the chosen gauge. To see how to guarantee this, let us rewrite Eqs. (3.72, 3.73) as follows:

$$\tilde{H}'^{(1)}(t) = \hat{H}^{(1)} + \hat{H}^{(1)}_{LS}(t) + \hat{H}^{(1)}_{X}(t) - \hbar \sum_{j=1}^{d^{(1)}} \left(\frac{d\theta_j(t)}{dt} \right) |\varphi^{(1)}_j(t)\rangle\langle\varphi^{(1)}_j(t)|, \tag{3.101}$$

$$\tilde{H}'^{(2)}(t) = \hat{H}^{(2)} + \hat{H}^{(2)}_{LS}(t) + \hat{H}^{(2)}_{X}(t) + \hbar \sum_{j=1}^{d^{(2)}} \left(\frac{d\theta_j(t)}{dt} \right) |\varphi^{(2)}_j(t)\rangle\langle\varphi^{(2)}_j(t)|. \tag{3.102}$$

If we add a dimensionless parameter $\varepsilon \in [0,1]$, such that $\hat{H}_{int} \to \varepsilon\hat{H}_{int}$ and make $\varepsilon \to 0$, for the new gauge we would obtain

$$\tilde{H}'^{(1)}(t) = \hat{H}^{(1)} - \hbar \sum_{j=1}^{d^{(1)}} \left(\frac{d\theta_j(t)}{dt} \right) |\varphi^{(1)}_j(t)\rangle_{bare}\langle\varphi^{(1)}_j(t)|_{bare}, \tag{3.103}$$

$$\tilde{H}'^{(2)}(t) = \hat{H}^{(2)} + \hbar \sum_{j=1}^{d^{(2)}} \left(\frac{d\theta_j(t)}{dt} \right) |\varphi^{(2)}_j(t)\rangle_{bare}\langle\varphi^{(2)}_j(t)|_{bare}. \tag{3.104}$$

where $|\varphi^{(k)}_j(t)\rangle_{bare} = e^{-\frac{i}{\hbar}\hat{H}^{(k)}(t-t_0)}|\varphi^{(k)}_j(t_0)\rangle$ is the free evolution of the initial Schmidt basis for $t \geq t_0$[u]. Observe that the phases are still relevant, but, despite being mathematically allowed, not all sets of phases are necessarily physically consistent with the expected behaviour in the absence of the interaction. Of course, if we constrain $\frac{d}{dt}\theta_j(t) = 0$ for all j, we automatically obtain $\tilde{H}'^{(k)}(t) = \hat{H}^{(k)}$. However, we can be more general: instead, if we require $\frac{d}{dt}\theta_j(t) = \alpha \in \mathbb{R}$ for all j, the limiting expressions above would provide equivalent conclusions, in the sense that they would still consistently describe the same local energy measurement differences since

$$\tilde{H}'^{(1)}(t) = \hat{H}^{(1)} - \hbar\alpha\hat{1}^{(1)}, \tag{3.105}$$

$$\tilde{H}'^{(2)}(t) = \hat{H}^{(2)} + \hbar\alpha\hat{1}^{(2)}, \tag{3.106}$$

and the additive constant $\hbar\alpha\hat{1}^{(k)}$ just equally shifts the energy spectrum, i.e., as long the phases are linear functions of time, such that $\theta_j(t) = \alpha t + c_0$ with $c_0 \in \mathbb{R}$ being an arbitrary constant for all j, the expected compatibility with the limiting behaviour is guaranteed.

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[u] As shown in Section (3.2), the perturbative series of the Schmidt basis elements are given by $|\varphi^{(k)}_j(t)\rangle = |\varphi^{(k)}_j(t)\rangle_{bare} + \varepsilon|\varphi^{(k)}_j(t)\rangle_1 + \mathcal{O}^{(k)}(\varepsilon^2)$.

Hence, in order to assure physical consistency, we must only consider gauges such that $\left\{\frac{d}{dt}\theta_j(t) = \alpha\right\}_j$ with $\alpha \in \mathbb{R}$. In this scenario, Eqs. (3.72, 3.73, 3.74, 3.75) simplify to

$$\tilde{H}'^{(1)}(t) = \tilde{H}^{(1)}(t) - \hbar\alpha\hat{1}^{(1)}, \tag{3.107}$$

$$\tilde{H}'^{(2)}(t) = \tilde{H}^{(2)}(t) + \hbar\alpha\hat{1}^{(2)}, \tag{3.108}$$

and

$$\langle\tilde{H}'^{(1)}(t)\rangle = \langle\tilde{H}^{(1)}(t)\rangle - \hbar\alpha, \tag{3.109}$$

$$\langle\tilde{H}'^{(2)}(t)\rangle = \langle\tilde{H}^{(2)}(t)\rangle + \hbar\alpha, \tag{3.110}$$

respectively. Interestingly, notice that, within this set of gauges, all the local effective Hamiltonians possess the same gap structure, while their expectation values simply differ from one another by an additive constant. Under these circumstances, if we identify the local physical internal energies as $\langle\tilde{H}^{(k)}(t)\rangle = U^{(k)}(t)$, even though different gauges would provide distinct absolute energy values, we guarantee identical energy measurement differences. Along these lines, the remaining freedom α just shifts the energy by $\pm\hbar\alpha$ and is analogous to the classical thermodynamic freedom in the definition of internal energy. (7)

In summary, despite the broad mathematical freedom, we were able to identify and fix the set of physically consistent phases, $\left\{\frac{d}{dt}\theta_j(t) = \alpha \in \mathbb{R}\right\}_j$, that recovers the expected limiting behaviour. In this sense, it is worth mentioning that such a procedure and reasoning explicitly demanded knowledge about the interaction $\hat{H}_{int}$ to obtain the correct physical phase gauge. Thus, in order to construct a local and consistent energy description for the subsystems, one cannot rely solely on local features (see (196) for a recent discussion). Finally, as long it is chosen a gauge that belongs to this relevant set, one can identify physical local internal energies up to an additive constant, such that the physical local effective Hamiltonians are guaranteed to possess invariant (unambiguous) spectral gaps.

3.6 Thermodynamics

In Section (2.3), we briefly introduced the general context and main motivations underlying the formulation of a thermodynamic theory for non-equilibrium quantum systems. We also stressed that its development is, currently, a work in progress and that several fundamental issues are still under scrutiny. In fact, the lack of consensus and understanding on some key aspects emphasize a real challenge to establishing the foundations of the theory and highlights the urgency of fostering discussion at the fundamental level. Along these lines, the most critical barrier lies in the proper identification of general quantum versions of the most basic classical thermodynamic quantities, such as internal energy, work, heat and entropy. On the one hand, the definitions of work and heat require both the previous recognition of physical internal energy and the understanding of the essential features that characterize these quantities; on the other, the concept of entropy and irreversibility, despite being a central concept in modern physics and several branches of science, remains elusive for general scenarios. Hence, it is unclear how to state the well-known laws of thermodynamics for situations whose both non-equilibrium processes and quantum features play essential roles. While the former is consistently contemplated in the formalism of stochastic thermodynamics, the latter is still obscure. One can find in the literature several proposals for accounting for these questions. However, most current approaches still rely on thermal states and baths, semi-classical asymmetrical descriptions and approximative regimes, which makes them not suitable for describing the thermodynamics within fully quantum (autonomous) systems.

Let us now briefly present and discuss part of the current efforts concerning the generalization of the usual equilibrium thermodynamic concepts and results to arbitrary non-equilibrium quantum systems. Also, when possible, we will consider our pure bipartite setup and mention how our approach fits into this context.

3.6.1 Remarks on thermal states

In thermodynamics, both classical and quantum, we are most of the time interested in describing and characterizing systems at equilibrium. These states are dynamical fixed points attained asymptotically in time and constrained by conserved physical properties. More frequently, however, it is focused on systems whose internal energy remains fixed. In those cases, the usual Gibbs canonical ensemble, given by

$$\hat{\rho}_{th} = \frac{e^{-\beta \hat{H}}}{Z}, \tag{3.111}$$

is the appropriate steady-state, where $\hat{H}$ is the Hamiltonian, $\beta = \frac{1}{k_B T}$ is the inverse of temperature T and $Z \equiv tr\{e^{-\beta \hat{H}}\}$ is the partition function[v]. Interestingly, by the usual Lagrange multipliers method, one can easily show that Eq. (3.111) is exactly the state that maximizes the von Neumann entropy S_{vN}[w], once assumed that the expectation value of the Hamiltonian, $\langle \hat{H} \rangle = tr\left\{\hat{\rho}\hat{H}\right\}$, is a constant quantity. From a more fundamental perspective, nevertheless, such states might be derived and justified by the usual statistical physics recipe of assuming that the system of interest is weakly interacting with a - much larger - heat bath and invoking the equal *a priori* probability postulate, which basically assumes that the whole bipartition is statistically described by the microcanonical ensemble. Essentially, assuming the total Hamiltonian given by Eq. (3.1), if the state of the whole system is maximally mixed, $\hat{\rho}^{(0)} = \frac{\hat{1}^{(0)}}{d^{(0)}}$, and $d^{(2)} \gg d^{(1)}$ with $\hat{H}_{int}$ negligible,

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[v] If more conserved quantities should be considered, then different steady-states are reached, and a generalized Gibbs ensemble (GGE) takes place.

[w] This quantity will be properly defined below.

one can show that

$$\hat{\rho}^{(1)} = tr_2\{\hat{\rho}^{(0)}\} = \frac{e^{-\beta \hat{H}^{(1)}}}{Z^{(1)}}. \tag{3.112}$$

Of course, once considered pure states for the whole system, it is not obvious if Eq. (3.112) should also be true or not. Along these lines, arguments on canonical typicality show that, in fact, the postulate above might be dismissed, i.e., if the whole system is restricted by a given arbitrary condition R such that $|\Psi\rangle \in \mathcal{H}^{(R)} \subseteq \mathcal{H}^{(0)} = \mathcal{H}^{(1)} \otimes \mathcal{H}^{(2)}$, it was shown that for almost every pure state $|\Psi\rangle$, the local state $\hat{\rho}^{(1)} = tr_2\{|\Psi\rangle\langle\Psi|\}$ of a sufficiently small subsystem ($d^{(1)} \ll d^{(2)}$) is approximately equal to $\hat{\rho}^{(1)} \approx tr_2\left\{\frac{\hat{1}^{(R)}}{d^{(R)}}\right\}$, where $\frac{\hat{1}^{(R)}}{d^{(R)}}$ is the maximally mixed state of the whole system, once considered the states consistent with the restriction. This result is completely general but can be directly connected to thermal states. One can show that as long R translates into the total internal energy being close to a fixed value, the subsystems are weakly-coupled, and the density of states of subsystem (2) increases approximately exponentially with energy, the local state $\hat{\rho}^{(1)}$ is approximately equal to the equilibrium state (197, 198), i.e.,

$$\hat{\rho}^{(1)} = tr_2\{|\Psi\rangle\langle\Psi|\} \approx \frac{e^{-\beta \hat{H}^{(1)}}}{Z^{(1)}}. \tag{3.113}$$

Despite powerful statements, these results are still restrictive to a very asymmetrical treatment and regime, and far from being applicable to many relevant scenarios within QT[x]. Clearly, thermal states are extremely useful and important, and one might still assume previous thermal states preparations regardless of the system's nature. However, the thermodynamic analysis of finite and quantum systems, in general, will have to deal with non-equilibrium states. Strictly speaking, the classical setting of two interacting subsystems in individual local thermal states are not allowed for pure bipartite systems: given $|\Psi\rangle$, the Schmidt decomposition, Eq. (3.3), guarantee that the local states - independently of the subsystems - must have the same spectrum $\{\lambda_j\}_j$, which means that the number of non-zero populations are bounded by the smallest dimension in question, i.e., if $\hat{H}^{(1,2)} \equiv \sum_{j=1}^{d^{(1,2)}} b_j^{(1,2)} |b_j^{(1,2)}\rangle\langle b_j^{(1,2)}|$ are the local bare Hamiltonians, our framework clearly shows that there is no pure state $|\Psi\rangle\langle\Psi|$ such that

$$\hat{\rho}^{(1)} = tr_2\{|\Psi\rangle\langle\Psi|\} = \sum_{j}^{d^{(1)}} \frac{e^{-\beta b_j^{(1)}}}{Z_1} |b_j^{(1)}\rangle\langle b_j^{(1)}|, \tag{3.114}$$

and

$$\hat{\rho}^{(2)} = tr_1\{|\Psi\rangle\langle\Psi|\} = \sum_{j}^{d^{(2)}} \frac{e^{-\beta b_j^{(2)}}}{Z_2} |b_j^{(2)}\rangle\langle b_j^{(2)}|, \tag{3.115}$$

simultaneously.

On the other hand, even if the whole system $\hat{\rho}^{(0)}$ is assumed (or previously prepared) to be mixed and thermal with a temperature T, once interaction within the bipartition becomes appreciable local divergences from Eq. (3.111) are expected to appear. Along

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[x] For instance, when considering systems of similar dimensionality $d^{(2)} \approx d^{(1)}$.

these lines, the understanding of the thermodynamic behaviour at the (ultra)strong coupling regime has also recently been investigated. The current approach is based on earlier work by (199) and consists of the definition of a local effective Hamiltonian for a subsystem interacting with a large reservoir, the so-called Hamiltonian of mean force (HMF), that guarantee the usual canonical Gibbs state form (see (156, 200) and (163) for further references), i.e., assuming $\hat{\rho}^{(0)} = \hat{\rho}^{(0)}_{th}$ one can show that the local state $\hat{\rho}^{(1)}$ can be cast as

$$\hat{\rho}^{(1)} = tr_2\{\hat{\rho}^{(0)}_{th}\} \equiv \frac{e^{-\beta \hat{H}^{(1)}_{eff}}}{Z^{(1)}_{eff}} \tag{3.116}$$

where $Z^{(1)}_{eff} \equiv tr_1\{e^{-\beta \hat{H}^{(1)}_{eff}}\}$ is the new partition function and

$$\hat{H}^{(1)}_{eff} := -k_B T\, ln(tr_2\{e^{-\beta \hat{H}^{(0)}}\}/tr_2\{e^{-\beta \hat{H}^{(2)}}\}), \tag{3.117}$$

is the HMF, that clearly depends on the temperature T and the interaction $\hat{H}_{int}$. Since the functional thermal structure in Eq. (3.116) is preserved, this formalism allows a straightforward connection with the usual equilibrium thermodynamic expressions and mathematical machinery, in particular the definition of effective versions of the thermodynamic potentials, such as the Helmholtz free energy, given by $F^{(1)}_{eff} \equiv -\beta^{-1} ln(Z^{(1)}_{eff})$.

In short, despite omnipresence and undeniable importance in equilibrium thermodynamics, the emergence and use of thermal states represent particular cases of more broad scenarios of quantum dynamic processes. In this sense, there are many open questions and it is imperative to develop a quantum thermodynamic formalism able to deal with arbitrary states, systems, non-thermal baths and general coupling regimes.

3.6.2 Remarks on quantum thermodynamic entropy

Along with the concept of energy, entropy has also reached the status of one of the most fundamental quantities in modern physics. Interestingly, despite being initially introduced in thermodynamics, its use transcended the scope of its initial conception, and now it is being used across several disciplines. Despite this universality, its understanding remains elusive, especially when considering questions regarding the second law and its extension to describe non-equilibrium quantum systems. Let us now briefly discuss the current status and approaches of entropy in the context of QT. For more discussions, see. (132)

3.6.2.1 General context

In Section (2.1), we briefly introduced the second law of thermodynamics, the notion of thermodynamic entropy and its intrinsic relationship with irreversibility. As we saw, essentially, it states that the entropy production of an isolated system, $\Sigma = \Delta S_{th}$, along any path, should increase or remain the same, i.e., $\Sigma \geq 0$, where the equality is satisfied if and only if reversible processes have taken place. From a pragmatical point of view, such a powerful statement imposes fundamental and universal constraints on any possible physical transformation. Further progress on the understanding of entropy, and thermodynamics in general, came along with contemporary developments in the study of non-equilibrium systems. In this sense, stochastic thermodynamics both pushed the boundaries of thermodynamics to once uncharted regimes and provided novel insights into the foundations of the theory. As mentioned earlier, in this context, entropy - and other relevant thermodynamic quantities - are fluctuating quantities defined and characterized at the individual phase space trajectory level. (10, 12, 133) If $p(q,t)$ is the probability of finding a given physical system in state q at time t, the stochastic entropy is simply defined by the following expression (133)

$$s(t) \equiv -k_B ln(p(q,t)), \tag{3.118}$$

Interestingly, such a formulation naturally implies that there will be some trajectories with negative entropy production, which is also implicit in the Fluctuation Theorems, in particular $\langle e^{-\frac{\Sigma}{k_B}} \rangle = 1$. Nevertheless, the usual second law statement is satisfied once considered an ensemble analysis and mean values, such that

$$S_{Gibbs}(t) \equiv -k_\beta \int dq\, p(q,t) ln(p(q,t)) = \langle s(t) \rangle, \tag{3.119}$$

where $S_{Gibbs}(t)$ is the well known Gibbs entropy (or Shannon entropy if k_B is not considered): this expression is well defined for any probability distribution $p(q,t)$ and it is commonly regarded as a proper choice for nonequilibrium extension of the thermodynamic entropy, S_{th}; in fact, if the system is at thermal equilibrium with inverse of temperature β, the probabilities are given by the equilibrium Boltzmann distribution $p_{eq}(q) = Z^{-1}(T)e^{-\beta E(q)}$, where $E(q)$ is the energy for the qth state, and the Gibbs expression above becomes equal to the usual thermodynamic entropy relation

$$S_{Gibbs} = \frac{1}{T}\left(\langle E \rangle - F(T)\right) = S_{th}, \tag{3.120}$$

where $\langle E \rangle$ is the system's internal energy, $F(T) \equiv -\beta^{-1}\, ln(Z(T))$ is the Helmholtz free energy and $Z(T) \equiv \int dq\, e^{-\beta E(q)}$ is the partition function; in addition, considering a proper identification of heat Q, one can show that

$$dS_{Gibbs} = \Sigma + d\Phi, \tag{3.121}$$

for arbitrary changes, where $\Sigma \geq 0$ is the positive entropy production and $d\Phi = \frac{dQ}{T}$ is the entropy flux due to heat exchange with a heat bath with temperature T. In short, once identified the Eq. (3.119) as the general quantifier of entropy, one recovers the usual thermodynamic expressions and the second law behaviour for both equilibrium and non-equilibrium scenarios.

3.6.2.1.1 Fully informational perspective

From now on, let us explicitly assume that $k_B = 1$[y]. The quantum counterpart of the Gibbs/Shannon entropy is given by the von Neumann entropy

$$S_{vN}[\hat{\rho}] \equiv -tr\left\{\hat{\rho} ln\left(\hat{\rho}\right)\right\}, \tag{3.122}$$

where $\hat{\rho}$ is the system's density matrix. Before discussing further, first, let us recall some of the basic properties of the Eq. (3.122) (39):

1. **Positivity:** $S_{vN}[\hat{\rho}] \geq 0$ for all $\hat{\rho}$. The equality is obtained if and only if the state is pure, i.e., $\hat{\rho} = |\psi\rangle\langle\psi|$;
2. **Unitary invariance:** $S_{vN}[\hat{\rho}] = S_{vN}[\hat{U}\hat{\rho}\hat{U}^{\dagger}]$ for any unitary $\hat{U}$;
3. **Subadditivity:** For bipartite systems described by $\hat{\rho}^{(0)}$ and reduced states $\hat{\rho}^{(1,2)} = tr_{2,1}\{\hat{\rho}^{(0)}\}$ we have the following inequality, $S_{vN}[\hat{\rho}^{(0)}] \leq S_{vN}[\hat{\rho}^{(1)}] + S_{vN}[\hat{\rho}^{(2)}]$. Equality is guaranteed only for uncorrelated systems, such that $\hat{\rho}^{(0)} = \hat{\rho}^{(1)} \otimes \hat{\rho}^{(2)}$.

In analogy with the classical definition of mutual information, from property 3. one might define its quantum counterpart as the following difference

$$I_{12} \equiv S[\hat{\rho}^{(0)}||\hat{\rho}^{(1)} \otimes \hat{\rho}^{(2)}] = S_{vN}[\hat{\rho}^{(1)}] + S_{vN}[\hat{\rho}^{(2)}] - S_{vN}[\hat{\rho}^{(0)}] \geq 0, \tag{3.123}$$

where $S[\hat{\rho}||\hat{\sigma}] = tr\{\hat{\rho}[ln(\hat{\rho}) - ln(\hat{\sigma})]\}$ is the quantum relative entropy. The expression above is clearly positive (due to the subadditivity) and quantifies the total correlations - classical *and* quantum - within the whole quantum system $\hat{\rho}^{(0)}$.

In the context of QT, Eq. (3.122) is the most commonly chosen candidate for quantifying quantum entropy. Its popularity is partially inherited by the success of Eq (3.119) in the classical domain, but also because it behaves properly for some key scenarios: again, if we consider thermal states, such the ones given by Eq. (3.111), it is easy to see that the Eq (3.122) automatically satisfy the thermodynamic entropy relation below

$$S_{vN}[\hat{\rho}_{th}] = -tr\left\{\hat{\rho}_{th} ln\left(\hat{\rho}_{th}\right)\right\} = \frac{1}{T}(U - F) = S_{th}, \tag{3.124}$$

where $U \equiv tr\left\{\hat{\rho}_{th}\hat{H}\right\} = \langle\hat{H}\rangle$ is identified as the internal energy and $F \equiv -\beta^{-1} ln(Z)$ is the Helmholtz free energy; also, if we consider a quantum system initially described by $\hat{\rho}(t_0)$ and weakly coupled to a thermal bath with temperature T, such that $\hat{\rho}_{th}$ is the system's asymptotic state, one can easily check the expression $S[\hat{\rho}(t)||\hat{\rho}_{th}] = -S_{vN}[\hat{\rho}(t)] + \frac{1}{T}\left(\langle\hat{H}\rangle(t) - F\right)$, where $\langle\hat{H}\rangle(t) = tr\left\{\hat{\rho}(t)\hat{H}\right\}$. Then, if $\hat{\rho}(t)$ is the state at instant t, by

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[y] At the end of the day, it does not influence our discussion.

identifying entropy production and heat as $\Sigma = -(S[\hat{\rho}(t)||\hat{\rho}_{th}] - S[\hat{\rho}(t_0)||\hat{\rho}_{th}])$ and $Q = tr\left\{(\hat{\rho}(t) - \hat{\rho}(t_0))\hat{H}\right\}$, respectively, we obtain

$$\Delta S_{vN} = \Sigma + \frac{1}{T}Q. \tag{3.125}$$

The positivity of Σ is assured by the fact that $S[\Lambda[\hat{\rho}]||\Lambda[\hat{\sigma}]] \leq S[\hat{\rho}||\hat{\sigma}]$ for CPTP maps $\Lambda[(.)]$: if $\hat{\rho}(t) = \Lambda_{t,t_0}[\hat{\rho}(t_0)]$ and since $\hat{\rho}_{th}$ is a fixed point for this dynamics, i.e., $\Lambda_{t,t_0}[\hat{\rho}_{th}] = \hat{\rho}_{th}$, we guarantee that $S[\Lambda_{t,t_0}[\hat{\rho}(t_0)]||\Lambda_{t,t_0}[\hat{\rho}_{th}]] = S[\hat{\rho}(t)||\hat{\rho}_{th}] \leq S[\hat{\rho}(t_0)||\hat{\rho}_{th}]$ and, therefore,

$$\Sigma = -(S[\hat{\rho}(t)||\hat{\rho}_{th}] - S[\hat{\rho}(t_0)||\hat{\rho}_{th}]) \geq 0. \tag{3.126}$$

Similar statements for entropy production can be made even if assuming slightly broader cases, such as considering explicitly Hamiltonian time-dependency. (56, 128)

Nevertheless, the use of the von Neumann entropy often comes along with a fully information-theoretic perspective of entropy production, in which the thermodynamic relevant scenarios mentioned above are seen as particular cases. Along these lines, irreversibility and, therefore, Σ, only appears once information is omitted (or becomes inaccessible) from a local point-of-view. Such reasoning was put forward by reference (127), but see (132) for further discussions. More specifically, if at $t = t_0$ a system of interest (1) is put into contact with another arbitrary system (2), such that $\hat{\rho}^{(0)}(t_0) = \hat{\rho}^{(1)}(t_0) \otimes \hat{\rho}^{(2)}(t_0)$, the local von Neumann entropy change $\Delta S_{vN}[\hat{\rho}^{(1)}] = S_{vN}[\hat{\rho}^{(1)}(t)] - S_{vN}[\hat{\rho}^{(1)}(t_0)]$ can be separated into

$$\Delta S_{vN}[\hat{\rho}^{(1)}] = S[\hat{\rho}^{(0)}(t)||\hat{\rho}^{(1)}(t) \otimes \hat{\rho}^{(2)}(t_0)] + tr_2\{(\hat{\rho}^{(2)}(t) - \hat{\rho}^{(2)}(t_0))ln(\hat{\rho}^{(2)}(t_0))\}, \tag{3.127}$$

where $\hat{\rho}^{(1,2)}(t) = tr_{2,1}\{\hat{\rho}^{(0)}(t)\}$ and $\hat{\rho}^{(0)}(t)$ evolves unitarily. While the second term from the right-hand side is identified as entropy flux $\Phi(t)$, entropy production is defined as

$$\Sigma(t) = S[\hat{\rho}^{(0)}(t)||\hat{\rho}^{(1)}(t) \otimes \hat{\rho}^{(2)}(t_0)], \tag{3.128}$$

such that the usual thermodynamic form $\Delta S_{vN}[\hat{\rho}^{(1)}] = \Sigma(t) + \Phi(t)$ is recovered. By construction, this quantity is non-negative $\Sigma(t) \geq 0$ for all t, with equality being satisfied if and only if the whole time-evolved state remains uncorrelated and subsystem (2) keeps unchanged throughout the dynamics, i.e., $\hat{\rho}^{(0)}(t) = \hat{\rho}^{(1)}(t) \otimes \hat{\rho}^{(2)}(t_0)$. Thus, essentially, $\Sigma(t)$ measures how far the actual whole system's state $\hat{\rho}^{(0)}(t)$ is from $\hat{\rho}^{(1)}(t) \otimes \hat{\rho}^{(2)}(t_0)$. Nevertheless, an information-theoretic interpretation of entropy production becomes more explicit if Eq. (3.128) above is cast as follows

$$\Sigma(t) = I_{12}(t) + S[\hat{\rho}^{(2)}(t)||\hat{\rho}^{(2)}(t_0)]. \tag{3.129}$$

Along these lines, $\Sigma(t)$ emerges from the lost information encoded both by the correlations within the whole system and the time evolution of the inaccessible subsystem (2), represented by $I_{12}(t)$ and $S[\hat{\rho}^{(2)}(t)||\hat{\rho}^{(2)}(t_0)]$, respectively. Notice that, ultimately, this perspective is very different from the classical second law notion: instead of focusing on quantifying the entropy change of the whole system, one concentrate on the analysis of the entropic dynamics - measured by the von Neumann entropy - of a local state. Having that in mind, despite inheriting some of the desired properties for a possible candidate of quantum thermodynamic entropy (at least for some paradigmatic scenarios), the use of the von Neumann entropy has some fundamental and challenging issues.

3.6.2.2 Issues of the von Neumann entropy

As mentioned earlier, in the classic context, the thermodynamic entropy of the whole system (commonly referred to as the universe), or the total entropy production, increases or remains the same for arbitrary dynamical processes. Thus, it is expected that any consistent quantum thermodynamic entropy definition, S_{Qth}, both generalizes the classical notions and capture this very general statement, i.e., $\Delta S_{Qth} \geq 0$. Interestingly, despite the prevailing use of the von Neumann entropy, it does not work as desired for arbitrary scenarios.

The unitary invariance of $S_{vN}[\hat{\rho}]$ (property **2.**) implies that for any isolated system, whose dynamics is fully characterized by the Schrödinger equation, the von Neumann entropy remains fixed, i.e.,

$$\hat{\rho}(t) = \hat{U}(t,t_0)\hat{\rho}(t_0)\hat{U}^{\dagger}(t,t_0) \;\Rightarrow\; \Delta S_{vN}[\hat{\rho}] = S_{vN}[\hat{\rho}(t)] - S_{vN}[\hat{\rho}(t_0)] = 0, \tag{3.130}$$

for all t. This strict equality is consistent with the second law, but there is no room for global entropy increases. Thus, in order to observe any entropic variation, it is required non-unitarity induced by some interaction with another system (at least in the first order of the interaction term, Eq. (3.50)). In fact, as we saw earlier, the local von Neumann entropies of subsystems within a bigger composite one might change in time. Along these lines, the general subadditivity of $S_{vN}[\hat{\rho}]$ (property **3.**) also represents a fundamental difference compared with the additivity observed in the thermodynamic entropy, i.e., the sum of the local entropies is equal to the whole's. For bipartite systems, for instance, along with Eq. (3.123), we see that the sum of local variations in their von Neumann entropies is equal to the change in the mutual information, such that

$$\Delta S_{vN}[\hat{\rho}^{(1)}] + \Delta S_{vN}[\hat{\rho}^{(2)}] = \Delta I_{12}, \tag{3.131}$$

where $\Delta I_{12} = I_{12}(t) - I_{12}(t_0)$ - a priori - could assume positive or negative values. Since $I_{12}(t)$ is necessarily positive for any t, in the special case of assuming initial uncorrelated systems ($\hat{\rho}^{(0)}(t_0) = \hat{\rho}^{(1)}(t_0) \otimes \hat{\rho}^{(2)}(t_0)$ and $I_{12}(t_0) = 0$), the expression above becomes $\Delta S_{vN}[\hat{\rho}^{(1)}] + \Delta S_{vN}[\hat{\rho}^{(2)}] = I_{12}(t) \geq 0$,which is similar to the thermodynamic statement but not general enough.

Let us now consider the setup described in Section (3.1): a generic pure bipartite system. In this context, the von Neumann entropy is commonly referred to as *entanglement* *entropy* since it directly measures the degree of entanglement between the partitions. First, from property **1.**, we know that the von Neumann entropy of pure states is null, thus for the whole system $S_{vN}[\hat{\rho}^{(0)}(t)] = 0$ throughout any - unitary - dynamics; then, given the symmetric description elucidated by the Schmidt decomposition (Eq. (3.3)), we have the local mixed states $\hat{\rho}^{(1,2)}(t)$ showed on Eqs. (3.5, 3.6), whose populations are given by the Schmidt coefficients squared $\{\lambda_j^2(t)\}_j$ and, therefore,

$$S_{vN}[\hat{\rho}^{(1)}(t)] = -\sum_{i=1}^{d^{(1)}} \lambda_i^2(t) ln\left(\lambda_i^2(t)\right) = S_{vN}[\hat{\rho}^{(2)}(t)] \tag{3.132}$$

for all t[z]. It is clear that if the Schmidt rank is equal to one, the whole system is separable $(|\Psi(t)\rangle = |\varphi^{(1)}(t)\rangle \otimes |\varphi^{(2)}(t)\rangle)$ and $S_{vN}[\hat{\rho}^{(1,2)}(t)] = 0$. In fact, given Eq. (3.123), for arbitrary bipartite systems, the local entropies are proportional to the mutual information quantifying the total correlation

$$S_{vN}[\hat{\rho}^{(1)}(t)] = S_{vN}[\hat{\rho}^{(2)}(t)] = \frac{1}{2} I_{12}(t) \geq 0, \tag{3.133}$$

and

$$\Delta S_{vN}[\hat{\rho}^{(1)}] = \Delta S_{vN}[\hat{\rho}^{(2)}] = \frac{1}{2}\Delta I_{12}, \tag{3.134}$$

which also clearly contrasts with the second law statement applied to a classical bipartition

$$\Delta S_{th}^{(1)} \geq -\Delta S_{th}^{(2)}. \tag{3.135}$$

In addition, the thermodynamic entropy is also directly linked with the energetics within a given process and, more specifically, the heat exchanged. Except for the cases already mentioned, namely when the systems are functionals of the Hamiltonians, and even more particular, for Gibbs states, it is not clear how to generalize a relationship between von Neumann entropy variation with energy flux. In fact, as we are going to discuss below, it also points-out a difficulty in identifying a candidate for quantum heat, since in classical thermodynamics heat is often defined as the energy exchange that also is accompanied by some entropic flux.

In short, despite the extensive use of the von Neumann entropy in QT and relative success for particular scenarios, it does not satisfy the expected properties for a proper microscopic generalization of the thermodynamic entropy, and it is not clear how to proceed. This, however, is already stressed by some authors. Along these lines, alternative proposals for a quantum thermodynamic entropy is represented by the observational (131, 201) and diagonal (129) ones, while the former relies on a coarse-graining process, the latter uses the von Neumann entropy form calculated considering only the instantaneous diagonal elements of the density matrix in the energy basis. In the end, such a lack

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[z] Of course, as mentioned earlier, any local functionals purely dependent on the Schmidt coefficients will be equal for both subsystems.

of agreement and understanding on this very basic quantity highlights the necessity of further investigations at the fundamental level. Otherwise, the thermodynamic role played by genuine quantum features, such as coherence and entanglement, will remain elusive, and developments of future quantum technologies will be affected.

3.6.3 Remarks on quantum work and heat

Once noticed that even the most basic concept of internal energy is still under scrutiny in the QT community, it should not be surprising the fact that the quantum versions of energy-based thermodynamic quantities, such as work and heat, are also elusive. Let us now briefly review work and heat in the general context of QT and, subsequently, consider them according to our effective internal energy description.

3.6.3.1 General context

For pedagogical purposes, let us divide the current approaches for defining quantum work and heat into two major distinct categories:

3.6.3.1.1 Operational approach

Among all thermodynamic quantities, quantum work is - by far - the most discussed one. On the one hand, given recent technological progress in the fabrication and manipulation of quantum systems, it is no surprise to find the concept of work in the spotlight of QT. Its complete understanding and control are one of the pinnacles of the field and is expected to fuel all sorts of technological applications, just like its classical counterpart did in the past. On the other hand, work has also been a central issue in former - although still contemporary - fundamental discussions concerning the generalization of thermodynamics to classical microscopic settings and the genesis of stochastic thermodynamics. (10, 12)

Unsurprisingly, this context served as an important stage for a considerable amount of efforts into the search for quantum work, especially for closed quantum systems. The usual setting consists of a quantum object, depicted by a state $\hat{\rho}(t)$, submitted to an externally controlled protocol, represented by a time-dependent Hamiltonian, such that $\hat{H}(t_0) \rightarrow \hat{H}(t_1)$ with $t_1 \geq t_0$. The closed time-evolution guarantees no other interactions and unitary dynamics, which commonly justify the interpretation of any energetic change as work $W(t)$ from/to the external agent, $\langle \hat{H}(t_1) \rangle - \langle \hat{H}(t_0) \rangle = W(t_1)$. In particular, the quest for quantum versions of FTs was a major driving force that helped to shed some light on very important aspects. For instance, it was argued that work W is not a fundamentally time-local entity, instead, it is characterized by processes and trajectories. Such reasoning is an extension of the classical thermodynamic conclusion that work is a path-dependent quantity and not a state function. This is often stated in the literature by the phrase "work is not an observable" (135), which means that work should not be simply understood and represented by a Hermitian operator $\hat{\Omega}$ such that $W := tr\{\hat{\Omega}\hat{\rho}\}$ and whose eigenvalues encode all the possible work measurements. Nevertheless, it is worth mentioning that it is not entirely clear if whether or not the concept of "work operator" is well-founded, which corresponds to an active debate in the field. (202–204) Furthermore, this route also encouraged discussions about possible meaningful definitions of quantum work fluctuations and the role of the measurement back-action: while the former demands a consistent stochastic description, i.e., a set $\{w_k\}_k$ of possible work outcomes and its distribution $P(w)$; the latter, highlight the invasive nature of measurements and its potential thermodynamic cost. Of course, both questions have their subtleties concerning foundational aspects of quantum mechanics. On the one hand, the definition of quantum analogous of classical stochastic trajectories is challenging and far from being trivial[aa]; on the other hand, discussions and criticisms concerning the underlying nature of the measurement postulate of quantum mechanics are as old as the first developments of the theory.

Along these lines, the orthodox approach of quantum stochastic trajectories in QT is based on the sequential projective measurements of the externally driven quantum system. Thus, stochasticity naturally emerges due to the probabilistic nature of the measurement process, and the set of outcomes establishes the dynamical path that the measured system follows during the intercalation of unitary time-evolution and measurements. While the drive plays the role of the classical external parameters changes, the measurement is analogous to random displacements due to noise. From this operational perspective, it became clear the possibility of defining the fluctuating work of performing a given protocol $\hat{H}(t_0) \to \hat{H}(t_1)$, as the difference of two projective energy measurements outcomes: if $E_k(t)$ is the kth eigenenergy at time t, hence fluctuating work is simply $w_{ji}(t_1) = E_j(t_1) - E_i(t_0)$. Therefore, the average work $\langle W(t_1) \rangle$ is directly obtained from an ensemble of protocol realizations. Interestingly, it was shown that the statistics $P_{TPM}(w)$ associated with such procedure, commonly known as the Two Projective Measurement protocol (TPM), both satisfy the classical FTs form (104, 206) and corresponds to the classical work distribution under the semi-classical limit, $P_{TPM}(w) \to P_{class}(w)$. (207, 208) Despite being the most popular approach and experimentally verifiable (73, 78, 79, 83, 88), the TPM scheme has some very important issues once considered initial coherent states (in the energy basis) and the unavoidable destructive effect of obtaining these informations. In such cases, the statistics of measurements (unsurprisingly) fail to capture the expected internal energy change of the unperturbed close quantum time-evolution, i.e., the first measurement eliminates all initial coherence and, therefore, influences the future state dynamics such that $\sum_{i,j} P_{TPM}(w_{ij}) w_{ij}(t_1) \neq \langle \hat{H}(t_1) \rangle - \langle \hat{H}(t_0) \rangle$[ab]. Additionally, the

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[aa] For instance, see (205) for a Bohmian perspective approach.

[ab] Of course, for non-coherent initial states, there is no such problem.

identification of energy measurements differences as representative values of work is disputable once considered open quantum systems. Such questions were partially addressed by a no-go theorem presented in (209), which states that there is no fluctuating work definition w and $P(w)$ that simultaneously satisfy the TPM statistics for non-coherent initial states ($P(w) = P_{TPM}(w)$), and $\sum_w P(w)w(t_1) = \langle \hat{H}(t_1)\rangle - \langle \hat{H}(t_0)\rangle$ for any initial state[ac]. The former condition explicitly assumes that the success of the TPM protocol in the FTs context is enough evidence for considering it as the correct distribution, while the latter is motivated by the assumption that the system is closed and, therefore, any energy exchange is due to work. Along these lines, other operational approaches are proposed in the literature, considering weak measurements, POVMS, etc. (210)

Also, in this context, the concept of *quantum heat* was introduced to account for the energetic price of performing a measurement. (105) In general, if a given state $|\psi\rangle$ is measured, it is induced an irreversible transformation $|\psi\rangle \rightarrow |\psi'\rangle$, such that $\langle\psi|\hat{H}|\psi\rangle \neq \langle\psi'|\hat{H}|\psi'\rangle$. This sudden change have no classical analogous and intrinsically depends on the eventual coherence in the chosen basis: of course, if the system is already in a given eigenstate of the measured observable, nothing will change. In this sense, the measurement apparatus is treated as the source of stochasticity for the time-evolution and plays a similar role played by thermal baths for the classical stochastic trajectories. From a thermodynamic point of view, heat is usually associated with irreversibility and entropic changes, which commonly justifies the identification of this energetic difference as a fully quantum analogous of heat, $q(t) := \langle\psi'|\hat{H}(t)|\psi'\rangle - \langle\psi|\hat{H}(t)|\psi\rangle$.

Finally, notice that operational perspectives of quantum thermodynamic quantities fundamentally depends on the assumption of external classical agents capable of performing certain protocols and measuring states. While the former is responsible for inducing a deterministic Hamiltonian time dependency, the latter introduces irreversible random outcomes. Consequently, and more importantly, such an approach prevents any further discussions concerning work and heat within fully isolated interacting quantum subsystems and, therefore, is not suitable for describing autonomous quantum machines (at least in any straightforward manner).

3.6.3.1.2 Dynamical approach

Instead of focusing on stochastic trajectories and fluctuating variables in an operational sense, one might be interested in a quantum dynamical description of these thermodynamic entities. Along these lines, work and heat are treated from an ensemble perspective and directly defined by changes in the internal energy, commonly identified by the expectation value of a given Hamiltonian $\langle\hat{H}(t)\rangle := tr\{\hat{H}(t)\hat{\rho}(t)\}$. Thus, given the

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[ac] In (210) there is a refinement and one more condition is considered, namely, the linearity of the distributions associated with different measurement protocols.

dynamical equation for both $\hat{\rho}(t)$ and $\hat{H}(t)$, in principle, one might be able to compute the thermodynamic quantities related to the followed dynamics. In this sense, the open quantum systems formalism provides a suitable mathematical framework for dealing both with the dynamics and energetics of general scenarios of interacting quantum systems.

Nevertheless, as mentioned earlier, it is not clear how to unambiguously identify quantum counterparts of work and heat. In fact, in the literature, there are several proposals and strategies for approaching these definitions from a dynamical point of view. However, most ideas are quantum versions of the following reasoning: consider a classical system with discrete states, indexed by j, the internal energy is simply given by the ensemble average $U_{cla} \equiv \sum_j E_j P_j$, where E_j is the energy of the jth state and P_j is its occupation probability, with $\sum_j P_j = 1$ (14, 211); it is also assumed that the energy states depends on the state of an external time-dependent control parameter $\eta(t)$, such that $E_j = E_j(\eta)$; thus, the internal energy change rate can be separated into two distinct categories

$$\frac{d}{dt} U_{cla} = \sum_j \frac{dE_j}{dt} P_j + \sum_j E_j \frac{dP_j}{dt}, \tag{3.136}$$

i.e., a change due to the state's energy alteration and a change coming from the occupation probability adjustment. The first contribution is interpreted as work rate ($\frac{d}{dt} W_{cla}(t)$) since it is the controlled energy transfering from/to the external agent, while the remaining change is identified as heat flow ($\frac{d}{dt} Q_{cla}(t)$) due to its relationship with transitioning states. Hence,

$$W_{cla}(t) := \sum_j \int_{t_0}^{t} ds \left(\frac{dE_j}{ds}\right) P_j = \sum_j \int_{t_0}^{t} ds \left(\frac{dE_j}{d\eta}\right) \left(\frac{d\eta}{ds}\right) P_j, \tag{3.137}$$

$$Q_{cla}(t) := \sum_j \int_{t_0}^{t} ds\, E_j \left(\frac{dP_j}{ds}\right), \tag{3.138}$$

and the first law of thermodynamics form is obtained $\frac{d}{dt} U_{cla}(t) = \frac{d}{dt} W_{cla}(t) + \frac{d}{dt} Q_{cla}(t)$. As just mentioned, such an approach provides an interesting route for defining the desired quantities. Nevertheless, purely quantum features do not allow a direct and unique analogy.

Along these lines, in (56) Alicki proposed a similar classification of quantum work and heat for open quantum systems weakly coupled to - possibly - N thermal reservoirs. It was also assumed a slowly driven Hamiltonian $\hat{H}(t) = \hat{H}_0 + \hat{h}(t)$, containing both the bare one and a time-dependent contribution representing the externally controlled parameters, given by $\hat{H}_0$ and $\hat{h}(t)$ respectively. Under these conditions, the state $\hat{\rho}(t)$ dynamics is described by a Markovian master equation in the usual Lindblad form, such that

$$i\hbar \frac{d}{dt} \hat{\rho}(t) = \left[\hat{H}(t), \hat{\rho}(t)\right] + \sum_k^N \hat{\mathfrak{D}}_t^{(k)} \hat{\rho}(t), \tag{3.139}$$

and $\hat{\mathfrak{D}}_t^{(k)}\hat{\rho}_{\beta_k} = 0$ for all k, where $\hat{\mathfrak{D}}_t^{(k)}$ is the non-unitary superoperator (also refered as dissipator) relative to the interaction with kth reservoir with inverse of temperature β_k and $\hat{\rho}_{\beta_k} = Z^{-1}e^{-\beta_k \hat{H}_0}$ is the usual Gibbs (thermal) state[ad]. The internal energy is recognized by the expectation value of $\hat{H}(t)$, i.e.,

$$U(t) := tr\{\hat{H}(t)\hat{\rho}(t)\}, \tag{3.140}$$

whose change rate is simply

$$\frac{d}{dt}U(t) = tr\left\{\frac{d}{dt}\hat{H}(t)\hat{\rho}(t)\right\} + tr\left\{\hat{H}(t)\frac{d}{dt}\hat{\rho}(t)\right\}. \tag{3.141}$$

In complete analogy with the classical case depicted by Eqs. (3.136-3.138), work is associated with the controlled energetic change, depicted by the Hamiltonian switch $\frac{d}{dt}\hat{H}(t)$, while heat is linked with the probabilities change encoded by the density operator dynamics $\frac{d}{dt}\hat{\rho}(t)$, i.e.,

$$W_1(t) := \int_{t_0}^{t} ds\, tr\left\{\frac{d}{ds}\hat{H}(s)\hat{\rho}(s)\right\}, \tag{3.142}$$

$$Q_1(t) := \int_{t_0}^{t} ds\, tr\left\{\hat{H}(s)\frac{d}{ds}\hat{\rho}(s)\right\}. \tag{3.143}$$

It is clear that such identifications automatically fulfil a quantum dynamical version of the first law, stated by $U(t) - U(t_0) = W_1(t) + Q_1(t)$[ae]. Besides, notice that heat $Q_1(t)$ does not depend on the unitary component of Eq. (3.139)[af], in such a way that $Q_1(t) = \sum_k^N \int_{t_0}^{t} ds\, tr\{\hat{H}(s)\hat{\mathfrak{D}}_t^{(k)}\hat{\rho}(s)\} = \sum_k^N Q_1^{(k)}(t)$, where $Q_1^{(k)}(t) \equiv tr\{\hat{H}(s)\hat{\mathfrak{D}}_t^{(k)}\hat{\rho}(s)\}$ is understood as the energy supplied by the kth reservoir. Thus, as expected, heat is the energy transferred due to the coupling with other systems, which also implies that $Q_1^{(k)}(t) = 0$ for all k iff the dynamics is unitary/closed. Work, on the other hand, explicitly relies on a semi-classical description for accounting for the external dynamical control and Hamiltonian time-dependency, which is assimilated by $\hat{h}(t)$. Thus, work is simply $W_1(t) \equiv \int_{t_0}^{t} ds\, tr\{\frac{d}{ds}\hat{h}(s)\hat{\rho}(s)\}$ and, therefore, vanishes iff the quantum system is isolated. As we can see, those definitions are consistent with the intuition behind their classical counterparts, however, it is not clear if they are still compatible with general dynamics, and - more importantly - it also prevents further discussions concerning the thermodynamics of autonomous quantum machines. Despite these issues, Alicki's definition proposal is widely accepted and used in the literature since their entropic predictions are consistent with the second law when considering weak-coupling and Markov approximations. Also, it is worth mentioning that alternative approaches of quantum work and

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[ad] The equality $\hat{\mathfrak{D}}_t^{(k)}\hat{\rho}_{\beta_k} = 0$ implies that $\hat{\rho}_{\beta_k}$ is a fixed-point relative to the kth reservoir. Essentially, it means that each reservoir alone would thermalize the system to its temperature.

[ae] The subscripts will be necessary to differentiate distinct work and heat definitions.

[af] Given the trace ciclic property, it is easy to see that $tr\left\{\hat{H}(t)\left[\hat{H}(t), \hat{\rho}(t)\right]\right\} = 0$.

heat also adopt the Eqs. (3.142, 3.143) forms, but instead of $\hat{H}(t)$ it is assumed different sorts of effective Hamiltonians. (164, 188–191, 212, 213)

Interestingly, note that the energy change rate splitting into two distinct terms is not unique, i.e., one might perform the trace in Eq. (3.140) on any conceivable basis, and separate its time derivative into two arbitrary components. For instance, if $\hat{H}(t) = \sum_j \epsilon_j(t)|\epsilon_j(t)\rangle\langle\epsilon_j(t)|$ is the instantaneous Hamiltonian spectral decomposition, we can rewrite Eq. (3.140) in the following way

$$U(t) \equiv \sum_j \epsilon_j(t) p_j(t), \tag{3.144}$$

where $p_j(t) := \langle\epsilon_j(t)|\hat{\rho}(t)|\epsilon_j(t)\rangle$ is the jth diagonal element of $\hat{\rho}(t)$ in the instantaneous Hamiltonian eigenbasis representation and quantify the probability of the system being in the state $|\epsilon_j(t)\rangle$. Then, in analogy with Eqs. (3.136-3.138), work and heat might be defined after the internal energy change rate

$$\frac{d}{dt}U(t) = \sum_j \frac{d\epsilon_j(t)}{dt} p_j(t) + \sum_j \epsilon_j(t) \frac{dp_j(t)}{dt}, \tag{3.145}$$

such that,

$$W_2(t) := \sum_j \int_{t_0}^{t} ds \, \frac{d\epsilon_j(s)}{ds} p_j(s), \tag{3.146}$$

$$Q_2(t) := \sum_j \int_{t_0}^{t} ds \, \epsilon_j(s) \frac{dp_j(s)}{ds}, \tag{3.147}$$

in a way that the first law equation form $U(t) - U(t_0) = W_2(t) + Q_2(t)$ is still satisfied. In general, the expressions above are different from the ones presented in Eqs. (3.142, 3.143). In particular, instead of being associated with the whole Hamiltonian change, work is only related to modifications in the energy spectrum $\frac{d\epsilon_j(t)}{dt}$ while heat depends on the dynamics of both the whole state $\hat{\rho}(t)$ and the energy eigenstates $\{|\epsilon_j(t)\rangle\}_j$, encoded by the populations $\{p_j(t)\}_j$. These quantities are directly related to Alicki's proposal in the following way

$$W_2(t) = W_1(t) - \sum_j \int_{t_0}^{t} ds \, \epsilon_j(s) \left(\frac{d}{ds} \left(\langle\epsilon_j(s)| \right) \hat{\rho}(s) |\epsilon_j(s)\rangle + \langle\epsilon_j(s)|\hat{\rho}(s) \frac{d}{ds} \left(|\epsilon_j(s)\rangle \right) \right), \tag{3.148}$$

$$Q_2(t) = Q_1(t) + \sum_j \int_{t_0}^{t} ds \, \epsilon_j(s) \left(\frac{d}{ds} \left(\langle\epsilon_j(s)| \right) \hat{\rho}(s) |\epsilon_j(s)\rangle + \langle\epsilon_j(s)|\hat{\rho}(s) \frac{d}{ds} \left(|\epsilon_j(s)\rangle \right) \right), \tag{3.149}$$

where it is clear that the only difference between both definitions is where the Hamiltonian basis change contribution is considered, and $U(t) - U(t_0) \equiv W_1(t) + Q_1(t) \equiv W_2(t) + Q_2(t)$. Conceptually, however, such approaches are very distinct and might predict conflicting scenarios. For instance, while for unitary processes $Q_1(t) = 0$ for all t, which implies that there is no heat involved, $Q_2(t)$ does not necessarily vanish for closed systems dynamics. In this sense, contrasting with the previous definition, the energy transferred by the external agent is divided into heat and work. Still, both approaches fundamentally rely on the classical picture that work is the energy externally provided in a controlled fashion.

Alternatively, instead of focusing on the energy basis with a prior role for work, more recently in (214, 215), it was suggested to use the instantaneous basis of the density matrix $\{|\phi_j(t)\rangle\}_j$ and concentrate on the identification of heat. Along these lines, if $\hat{\rho}(t) = \sum_j \varrho_j(t)|\phi_j(t)\rangle\langle\phi_j(t)|$ is the time-local spectral decomposition of $\hat{\rho}(t)$, Eq. (3.140) can also be written as

$$U(t) \equiv \sum_j \varepsilon_j(t)\varrho_j(t), \tag{3.150}$$

where $\{\varrho_j(t)\}$ are the instantaneous populations of $\hat{\rho}(t)$ and $\varepsilon_j(t) := \langle\phi_j(t)|\hat{H}(t)|\phi_j(t)\rangle$ is interpreted as the energy relative to the jth pure state $|\phi_j(t)\rangle$. Then, the energy change rate can be divided into

$$\frac{d}{dt}U(t) = \sum_j \frac{d\varepsilon_j(t)}{dt}\varrho_j(t) + \sum_j \varepsilon_j(t)\frac{d\varrho_j(t)}{dt} \tag{3.151}$$

and, again in analogy with Eqs. (3.136-3.138), work and heat might be defined as

$$W_3(t) := \sum_j \int_{t_0}^{t} ds\, \frac{d\varepsilon_j(s)}{ds}\varrho_j(s), \tag{3.152}$$

$$Q_3(t) := \sum_j \int_{t_0}^{t} ds\, \varepsilon_j(s)\frac{d\varrho_j(s)}{ds}, \tag{3.153}$$

such that $U(t) - U(t_0) = W_3(t) + Q_3(t)$. Hence, heat is associated with changes in the distribution of pure states $\left\{\frac{d}{dt}\varrho_j(t)\right\}_j$ while the remaining part, depending on the dynamics of both Hamiltonian $\hat{H}(t)$ and instantaneous basis $\{|\phi_j(t)\rangle\}_j$, is identified as work. Such division is motivated by the common recognition of the von Neumann entropy $S_{vN}(t) := -\sum_j \varrho_j(t)ln(\varrho_j(t))$ as the natural extension of thermodynamic entropy and the classical relationship between heat flux and entropy variation. Classically, heat is the portion of energy exchange accompanied by the flow of entropy into/from the system, while work is the energetic contribution that does not generate any entropic changes. Along these lines, since $\frac{d}{dt}S_{vN}(t) := -\sum_j \frac{d\varrho_j(t)}{dt}ln(\varrho_j(t))$, heat is associated with the non-unitary part of the system dynamics and, more specifically, identified by the energetic change that also functionally depends on $\frac{d\varrho_j(t)}{dt}$. Thus, if the time-evolution is unitary we would automatically have both $\frac{d}{dt}S_{vN}(t) = 0$ and $Q_3(t) = 0$ and, therefore, all energetic exchange would be due to work, $U(t) - U(t_0) = W_3(t)$. Also, it would guarantee the agreement between $W_3(t)$ and $W_1(t)$. Interestingly, this approach does not fundamentally require a semi-classical picture: even if the Hamiltonian $\hat{H}(t)$ is kept constant, for general open system dynamics the basis $|\phi_j(t)\rangle$ might change in such a way that $\frac{d\varepsilon_j(t)}{dt} \neq 0$ and work $W_3(t)$ is not necessarily null for fully quantum interacting subsystems. It is worth mentioning that in (216) was presented a simple example where $Q_3(t) = 0$ for all t while $\frac{d}{dt}S_{vN}(t) \neq 0$, which motivate the authors to argue that this may constitute a possible inadequacy between the thermodynamic argument and the definitions above.

Hence, despite having a similar thermodynamic grounding and interesting individual characteristics, all these proposals do not agree with each other in most cases. Naturally, different definitions may predict radically distinct thermodynamic scenarios. In particular, notice that the root of their divergence is due to the initial arbitrary basis representation choice for $U(t)$, which affects the contributions splitting and identification. Besides, it is also clear that coherence must be taken into account, i.e., in general $[\hat{\rho}(t), \hat{H}(t)] \neq 0$ and the quantum coherence - in any basis choice - plays an indispensable role in the energetic changes. For instance, even though non-diagonal elements of $\hat{\rho}(t_0)$ in the Hamiltonian basis at a given instant t_0, written as $\langle \epsilon_j(t_0)|\hat{\rho}(t_0)|\epsilon_k(t_0)\rangle$ with $j \neq k$, do not instantaneously contribute to the internal energy $U(t_0)$[ag], their dynamics are - in general - coupled with the populations $\langle \epsilon_j(t)|\hat{\rho}(t)|\epsilon_j(t)\rangle$[ah], which means that they are relevant for $U(t)$ at latter times ($t \geq t_0$). In other words, all density matrix elements are essential for accounting for the energetic change of any given quantum system. Interestingly, in the classical limit, such contributions become negligible in a way that these ambiguities disappear and the previous definitions converge to compatibility. In this sense, it is not obvious if such additional quantities should be interpreted as work-like or heat-like variations and, since there is no classical analogous of coherence, classical thermodynamics does not provide any direct instruction on how to deal with them. In fact, it is not even clear if coherence should be tied to such roles. Most of the literature implicitly assumes that either coherence is shared between both quantities or belongs to one of them, i.e., is commonly assumed a priori the classical thermodynamic structure of complementary ingredients. The classical first law states that $dU \equiv \delta W + \delta Q$, in a way that once defined work or heat, it is automatically established the remaining part. Thus, it is important to highlight that there is still room for disputing this assumption at the quantum level. Along these lines, as an alternative approach, (137) proposed a redefinition of the first law where the coherence energetic contribution, given by δC, is completely separated from the notions of work and heat, such that $U \equiv \delta W + \delta Q + \delta C$.

In summary, discussions on quantum counterparts of thermodynamic quantities are still in their early stages and far from being settled. This, of course, corresponds to a core conceptual issue for the development of a fully quantum thermodynamics theory

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[ag] Since $\hat{H}(t) = \sum_j \epsilon_j(t)|\epsilon_j(t)\rangle\langle\epsilon_j(t)|$, it is easy to see that

$$U(t) = tr\{\hat{H}(t)\hat{\rho}(t)\} = \sum_j \epsilon_j(t)\langle\epsilon_j(t)|\hat{\rho}(t)|\epsilon_j(t)\rangle.$$

[ah] For some specific situations, their dynamics might be decoupled, e.g., Davies maps.

and has a direct impact on the design and operation of effective quantum devices. The most popular routes offer either an operational framework or a semi-classical description, which are - essentially - phenomenological approaches in spirit and do not consistently apply for several scenarios of interest. Especially those that demand a more symmetrical thermodynamic treatment of all considered parties.

3.6.3.2 Road to effective work and heat

As mentioned earlier, in addition to not being clear which thermodynamic role is played by genuine quantum phenomena, it is also mandatory a previous identification of internal energy in order to properly recognize quantum versions of work and heat. Such fundamental ambiguities emphasize the urgency of careful examination of these quantities at the conceptual level. In particular, it is imperative the identification of the essential features of what exactly characterizes work and heat. Along these lines, in Section (3.4.1.1), we argued that the local effective Hamiltonians $\tilde{H}^{(1,2)}(t)$ provide a promising and suitable candidate for quantifying the subsystems internal energy $U^{(k)}(t) := \langle \tilde{H}^{(k)}(t) \rangle$, in a way that is local, additive ($\frac{d}{dt}U^{(1)}(t) = -\frac{d}{dt}U^{(2)}(t)$) and applicable to *arbitrary* scenarios. Hence, it also provides a starting point for discussing a general, exact and symmetrical understanding of work and heat along with any dynamical processes. This approach naturally allows the energetic characterization that transcends the usual asymmetric thermodynamic description and restrictive regimes, such as weakly coupled systems and markovian dynamics. Here, nevertheless, we do not propose fixed definitions for these quantities. Instead, we advocate that the previously presented work and heat forms from a dynamical point of view might be well adapted for our local internal energy identification.

The local internal energy dynamics for each subsystem is simply $\frac{d}{dt}U^{(k)}(t) = \frac{d}{dt}tr_k\{\tilde{H}^{(k)}(t)\hat{\rho}^{(k)}(t)\}$. From previous discussions, it becomes clear that this kind of expression can be consistently divided into two components in several distinct ways that still correspond to the first law structure[ai]. Then, we are always allowed to write the following expression

$$\frac{d}{dt}U^{(k)}(t) = \frac{d}{dt}\mathbb{W}^{(k)}(t) + \frac{d}{dt}\mathbb{Q}^{(k)}(t), \tag{3.154}$$

where $\mathbb{W}^{(k)}(t)$ and $\mathbb{Q}^{(k)}(t)$ are identified as the effective work and effective heat flowing from/to subsystem (k), respectively. Furthermore, the symmetrical treatment of both parts and internal energy additivity imply that all net energetic exchange involved during the whole system dynamics should sum up to zero, i.e.,

$$\frac{d}{dt}\mathbb{W}(t) + \frac{d}{dt}\mathbb{Q}(t) = 0, \tag{3.155}$$

[ai] Here we will assume a priori the usual first law structure.

where $\mathbb{W}(t) = \mathbb{W}^{(1)}(t) + \mathbb{W}^{(2)}(t)$ and $\mathbb{Q}(t) = \mathbb{Q}^{(1)}(t) + \mathbb{Q}^{(2)}(t)$ are the respective net work and net heat transferred throughout the described process.

From Eqs. (3.142, 3.143) one might approach these quantities according to Alicki's proposal in the following straightforward way

$$\mathbb{W}_1^{(k)}(t) := \int_{t_0}^{t} ds\, tr_k \left\{ \frac{d}{ds} \tilde{H}^{(k)}(s) \hat{\rho}^{(k)}(s) \right\} = \sum_{j=1}^{d^{(1)}} \int_{t_0}^{t} ds\, \lambda_j^2(s) \langle \varphi_j^{(k)}(s) | \frac{d}{ds} \tilde{H}^{(k)}(s) | \varphi_j^{(k)}(s) \rangle, \tag{3.156}$$

$$\mathbb{Q}_1^{(k)}(t) := \int_{t_0}^{t} ds\, tr_k \left\{ \tilde{H}^{(k)}(s) \frac{d}{ds} \hat{\rho}^{(k)}(s) \right\} = \sum_{j=1}^{d^{(1)}} \int_{t_0}^{t} ds\, \frac{d\lambda_j^2(s)}{ds} \langle \varphi_j^{(k)}(s) | \tilde{H}^{(k)}(s) | \varphi_j^{(k)}(s) \rangle, \tag{3.157}$$

where work is the energy exchange associated with the local effective Hamiltonian dynamics and heat is related to the local state change. Given Eq. (3.18), it is clear that work $\mathbb{W}_1^{(k)}(t)$ is a direct outcome of the time-dependency induced by the interaction between the subsystems and, therefore, does not require any ad hoc, external agent for describing it. In fact, the bare Hamiltonian $\hat{H}^{(k)}$ plays no role in this energetic exchange since $\hat{H}^{(k)} = cte$ and $\mathbb{W}_1^{(k)}(t) := \int_{t_0}^{t} ds\, tr_k \left\{ \frac{d}{ds} \left(\hat{H}_{LS}^{(k)}(s) + \hat{H}_X^{(k)}(s) \right) \hat{\rho}^{(k)}(s) \right\}$. Also, it intrinsically bound heat $\mathbb{Q}_1^{(k)}(t)$ with entanglement variation due to its explicitly functional dependency on the population dynamics $\left\{ \frac{d\lambda_j^2(t)}{dt} \right\}_j$. Additionally, in contrast with the classical equilibrium thermodynamic scenario, it is also clear that the net work $\mathbb{W}_1(t)$ and net heat $\mathbb{Q}_1(t)$ are not individually null for general situations. Thus, for instance, the heat flowing from subsystem (1) is not necessarily translated into the heat absorbed by subsystem (2), i.e., $\mathbb{Q}_1(t) = \mathbb{Q}_1^{(1)}(t) + \mathbb{Q}_1^{(2)}(t) \neq 0$. Finally, it is easy to show that

$$\langle \varphi_j^{(k)}(t) | \frac{d}{dt} \tilde{H}^{(k)}(t) | \varphi_j^{(k)}(t) \rangle = \frac{d}{dt} \left(\langle \varphi_j^{(k)}(t) | \tilde{H}^{(k)}(t) | \varphi_j^{(k)}(t) \rangle \right), \tag{3.158}$$

for all t and, therefore, that there is an equality between Alicki's proposal and the form presented in Eqs. (3.152, 3.153). In such a case, the heat $\mathbb{Q}_3^{(k)}(t)$ experienced by subsystem (k) is directly related to changes in the populations of the local state $\hat{\rho}^{(k)}(t)$, and work is assigned to the remaining energetic contribution due to the local effective Hamiltonian dynamics and instantaneous basis $\{|\varphi_j^{(k)}(t)\rangle\}_j$ variation. Hence

$$\mathbb{W}_1^{(k)}(t) = \sum_{j=1}^{d^{(1)}} \int_{t_0}^{t} ds\, \lambda_j^2(s) \frac{d}{dt} \left(\langle \varphi_j^{(k)}(s) | \tilde{H}^{(k)}(s) | \varphi_j^{(k)}(s) \rangle \right) = \mathbb{W}_3^{(k)}(t), \tag{3.159}$$

$$\mathbb{Q}_1^{(k)}(t) = \sum_{j=1}^{d^{(1)}} \int_{t_0}^{t} ds\, \frac{d\lambda_j^2(s)}{ds} \langle \varphi_j^{(k)}(s) | \tilde{H}^{(k)}(s) | \varphi_j^{(k)}(s) \rangle = \mathbb{Q}_3^{(k)}(t), \tag{3.160}$$

in contrast with what we would have obtained if we just had considered the local bare Hamiltonians[aj].

[aj] By hypothesis, we consider constant local bare Hamiltonians $\hat{H}^{(k)}$. Thus, the previous equality would not be satisfied, i.e., $0 = \langle \varphi_j^{(k)}(t) | \frac{d}{dt} \hat{H}^{(k)} | \varphi_j^{(k)}(t) \rangle \neq \frac{d}{dt} \left(\langle \varphi_j^{(k)}(t) | \hat{H}^{(k)} | \varphi_j^{(k)}(t) \rangle \right)$.

Alternatively, one might define work and heat in analogy with the procedure presented along with Eqs. (3.146, 3.147). If

$$\tilde{H}^{(k)}(t) \equiv \sum_{j=1}^{d^{(k)}} \tilde{\epsilon}_j^{(k)}(t) |\tilde{\epsilon}_j^{(k)}(t)\rangle\langle\tilde{\epsilon}_j^{(k)}(t)| \tag{3.161}$$

is the instantaneous local effective Hamiltonian spectral decomposition, where $\{\tilde{\epsilon}_j^{(k)}(t)\}_j$ are the time-local effective eigenenergies and $\{|\tilde{\epsilon}_j^{(k)}(t)\rangle\}_j$ are their eigenstates, it is clear that the effective internal energy can be cast as

$$U^{(k)}(t) = \langle \tilde{H}^{(k)}(t)\rangle = \sum_{j=1}^{d^{(k)}} \tilde{\epsilon}_j^{(k)}(t) \langle\tilde{\epsilon}_j^{(k)}(t)|\hat{\rho}^{(k)}(t)|\tilde{\epsilon}_j^{(k)}(t)\rangle. \tag{3.162}$$

Then, work $\mathbb{W}_2^{(k)}(t)$ and heat $\mathbb{Q}_2^{(k)}(t)$ could be identified as

$$\mathbb{W}_2^{(k)}(t) = \sum_{j=1}^{d^{(k)}} \int_{t_0}^{t} ds\, \frac{d\tilde{\epsilon}_j^{(k)}(s)}{ds} \langle\tilde{\epsilon}_j^{(k)}(s)|\hat{\rho}^{(k)}(s)|\tilde{\epsilon}_j^{(k)}(s)\rangle, \tag{3.163}$$

$$\mathbb{Q}_2^{(k)}(t) = \sum_{j=1}^{d^{(k)}} \int_{t_0}^{t} ds\, \tilde{\epsilon}_j^{(k)}(s) \frac{d}{ds}\left(\langle\tilde{\epsilon}_j^{(k)}(s)|\hat{\rho}^{(k)}(s)|\tilde{\epsilon}_j^{(k)}(s)\rangle\right), \tag{3.164}$$

such that the former is only associated with changes in the local effective Hamiltonian spectrum, instead of the whole operator, and the latter is related to the dynamics of its respective local state $\hat{\rho}^{(k)}(t)$ and basis $\{|\tilde{\epsilon}_j^{(k)}(t)\rangle\}_j$. Again, the equality presented in Eq. (3.155) above is guarateed by construction and there is no reason why the net work $\mathbb{W}_2(t)$ and net heat $\mathbb{Q}_2(t)$ should be individually null for general cases.

Thus, as presented above, the definition of the local effective internal energies $U^{(k)}(t) = \langle \tilde{H}^{(k)}(t)\rangle$ provides a consistent foundation for discussing work and heat and the first law in an exact, symmetrical and general manner. This, however, is not enough. As mentioned before, it is imperative to encourage in-depth investigations at the conceptual level. In particular, a focus on questions concerning the identification of what are the essential features that fundamentally characterizes work and heat is particularly needed. Otherwise, the energetic contribution of coherence will remain elusive and arbitrarily considered into potential candidates.

3.7 Proof of principle

To illustrate the concepts presented in this chapter, let us now apply our formalism for describing the energetic exchange of a simple - but paradigmatic - example of two interacting qubits as a proof of principle. Of course, a priori, this method applies to any quantum system, as long we perform a bipartition.

Suppose the system is described by the following Hamiltonian

$$\hat{H}^{(0)} := \hbar\frac{\omega_1}{2}\hat{\sigma}_z^{(1)} \otimes \hat{1}^{(2)} + \hat{1}^{(1)} \otimes \hbar\frac{\omega_2}{2}\hat{\sigma}_y^{(2)} + \hbar g\left(\hat{\sigma}_x^{(1)} \otimes \hat{\sigma}_y^{(2)}\right) \in \mathcal{L}(\mathcal{H}^{(0)}), \tag{3.165}$$

where $\hat{H}^{(1)} \equiv \hbar\frac{\omega_1}{2}\hat{\sigma}_z^{(1)}$ and $\hat{H}^{(2)} \equiv \hbar\frac{\omega_2}{2}\hat{\sigma}_y^{(2)}$ are the local bare Hamiltonians, $\hat{H}_{int} \equiv \hbar g\left(\hat{\sigma}_x^{(1)} \otimes \hat{\sigma}_y^{(2)}\right)$ is the interaction term, $\hat{\sigma}_{x,y,z}$ are the usual Pauli matrices, g is the coupling constant, and $\hbar\omega_{1,2}$ are the energy gaps for $\hat{H}^{(1,2)}$. Since we are dealing with two qubits, we have $d^{(0)} := dim(\mathcal{H}^{(0)}) = 4$ and $d^{(1,2)} := dim(\mathcal{H}^{(1,2)}) = 2$. Hence, for every time t, the whole system state will be written - in general - as

$$|\Psi(t)\rangle = \lambda_1(t)|\varphi_1^{(1)}(t)\rangle \otimes |\varphi_1^{(2)}(t)\rangle + \lambda_2(t)|\varphi_2^{(1)}(t)\rangle \otimes |\varphi_2^{(2)}(t)\rangle. \tag{3.166}$$

Given an initial state $|\Psi(0)\rangle$, it will evolve in time according to $|\Psi(t)\rangle = \hat{\mathcal{U}}(t)|\Psi(0)\rangle$, where $\hat{\mathcal{U}}(t) = e^{-\frac{i}{\hbar}\hat{H}^{(0)}t} \in \mathcal{L}(\mathcal{H}^{(0)})$ is the time-evolution operator. Conveniently, since the bare Hamiltonian of subsystem (2) commutes with the interaction term, $[\hat{H}^{(2)}, \hat{H}_{int}] = 0$, $\hat{\mathcal{U}}(t)$ simplifies to

$$\hat{\mathcal{U}}(t) = e^{-i\left(\frac{\omega_1}{2}\hat{\sigma}_z^{(1)}\otimes\hat{1}^{(2)}+g\left(\hat{\sigma}_x^{(1)}\otimes\hat{\sigma}_y^{(2)}\right)\right)t}e^{-i\frac{\omega_2}{2}\hat{\sigma}_y^{(2)}t}, \tag{3.167}$$

which also implies that $[\hat{H}^{(2)},\hat{\mathcal{U}}(t)] = 0$[ak]. Thus, if $\hat{\sigma}_y^{(2)}|\pm_y^{(2)}\rangle = \pm|\pm_y^{(2)}\rangle$ and $\hat{V}(t) := e^{-i\left(\frac{\omega_1}{2}\hat{\sigma}_z^{(1)}\otimes\hat{1}^{(2)}+g\left(\hat{\sigma}_x^{(1)}\otimes\hat{\sigma}_y^{(2)}\right)\right)t}$, then

$$\hat{\rho}^{(2)}(t) = e^{i\frac{\omega_2}{2}\hat{\sigma}_y^{(2)}t}tr_1\{\hat{V}^{\dagger}(t)|\Psi(0)\rangle\langle\Psi(0)|\hat{V}(t)\}e^{-i\frac{\omega_2}{2}\hat{\sigma}_y^{(2)}t} \tag{3.168}$$

and, therefore,

$$\langle\pm_y^{(2)}|\hat{\rho}^{(2)}(t)|\pm_y^{(2)}\rangle = \langle\pm_y^{(2)}|\hat{\rho}^{(2)}(0)|\pm_y^{(2)}\rangle \tag{3.169}$$

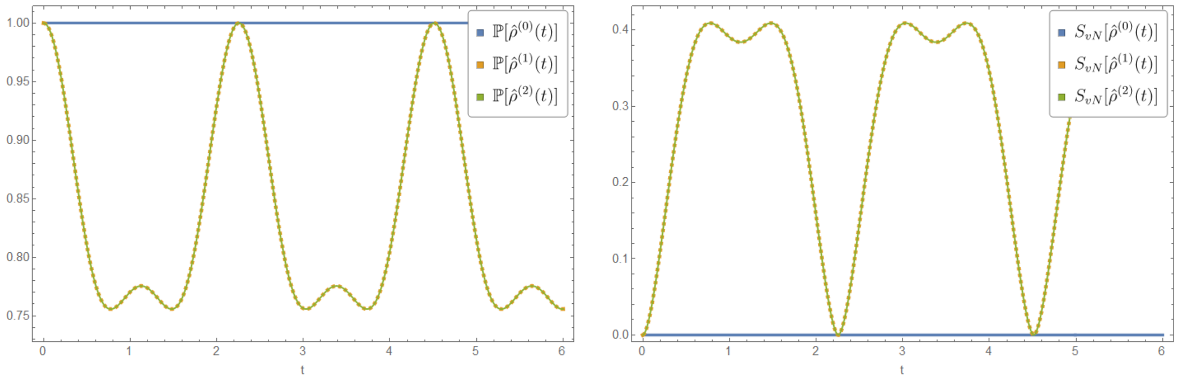
for all t, i.e., the populations of $\hat{\rho}^{(2)}(t)$ in the $\hat{\sigma}_y^{(2)}$ basis, $\{|\pm_y^{(2)}\rangle\}$, are constant during the whole dynamics, while the non-diagonal elements $\langle\mp_y^{(2)}|\hat{\rho}^{(2)}(t)|\pm_y^{(2)}\rangle$ may evolve independently. Notice this is not true for qubit (1), since $[\hat{H}^{(1)}, \hat{H}_{int}] \neq 0$, a priori, the change of all of its density matrix elements are coupled intrinsically with one another. Interestingly, despite their different dynamics, both qubits are guaranteed to maintain their equal purities during the whole time evolution. If $\mathbb{P}[\hat{\sigma}] \equiv tr\{\hat{\sigma}^2\}$ is the purity of a state $\hat{\sigma}$, then it is clear that $\mathbb{P}[\hat{\rho}^{(0)}(t)] = 1$ - given $\hat{\rho}^{(0)}(t) \equiv |\Psi(t)\rangle\langle\Psi(t)|$ is a pure state for all t - while $\mathbb{P}[\hat{\rho}^{(1)}(t)] = \mathbb{P}[\hat{\rho}^{(2)}(t)] = \lambda_1^4(t) + \lambda_2^4(t) \leq 1$. The local purity changes also reflect the modification in the entanglement degree between the qubits. As mentioned in Section (3.6.2.2), in this context, the von Neumann entropy (or entanglement entropy) represents a direct measure of the entanglement within the bipartition. Under these circumstances, while the whole system's von Neumann entropy is null throughout the dynamics (since it is pure), both subsystems are guaranteed to possess the same value for their von Neumann entropy, i.e., $S_{vN}[\hat{\rho}^{(0)}(t)] = 0$ and $S_{vN}[\hat{\rho}^{(1)}(t)] = S_{vN}[\hat{\rho}^{(2)}(t)] = -\lambda_1^2(t)ln\left(\lambda_1^2(t)\right) - \lambda_2^2(t)ln\left(\lambda_2^2(t)\right)$ for all t.

The temporal evolution of this simple physical system can be easily checked by numerical analysis. Let us suppose initial uncorrelated states, such that

$$|\Psi(0)\rangle = |\varphi^{(1)}(0)\rangle \otimes |\varphi^{(2)}(0)\rangle \tag{3.170}$$

[ak] If $\hat{A}$ and $\hat{B}$ commute, then $e^{\hat{A}+\hat{B}} = e^{\hat{A}}e^{\hat{B}}$.

with $|\varphi^{(k)}(0)\rangle = a^{(k)}|+_z^{(k)}\rangle + b^{(k)}|-_z^{(k)}\rangle$[al]. Thus, Figure 1a shows how the qubits purity oscillates between 1 and < 1, which indicates their continuously changing from pure to mixed states. Additionally, it is clear that the whole system's state also oscillates from the initial product to entangled states. In this sense, Figure 1b depicts the dynamical behaviour of the von Neumann entropies and illustrates that both quantities are, indeed, correlated. As expected, whenever the local density matrices are pure, their von Neumann entropies are equally null, while the maximum entanglement is obtained when their purities reach their minimum values.



(a) Purity

(b) von Neumann entropy

Figure 1 – **(a)** Purity dynamics for two interacting qubits. While the whole system maintains pure for all t, both qubits oscillate continuously between pure and mixed states with equal purity; **(b)** Dynamical behaviour of the von Neumann entropies. On the one hand, given $\hat{\rho}^{(0)}(t) \equiv |\Psi(t)\rangle\langle\Psi(t)|$, the whole system's von Neumann entropy maintains null throughout the unitary dynamics. On the other hand, the equal qubits' von Neumann entropies illustrate the oscillation between the degree of entanglement within the bipartition. For the computation of all the plots, it was assumed $a^{(1)} = (5)^{-1/2}, b^{(1)} = 2(5)^{-1/2}$, $a^{(2)} = (10)^{-1/2}$ and $b^{(2)} = 3(10)^{-1/2}$ for the initial states, $\hbar \equiv 1$, $\omega_1 = 1$, $\omega_2 = 5$ and $g = 1.3$.

Source: By the author.

More importantly, given that the populations of $\hat{\rho}^{(2)}$ in the $\hat{H}^{(2)}$ basis are time-invariant, the expectation value of the bare Hamiltonian, $\langle\hat{H}^{(2)}\rangle(t) \equiv tr_2\{\hat{H}^{(2)}\hat{\rho}^{(2)}(t)\} = \langle\Psi(t)|\hat{H}^{(2)}|\Psi(t)\rangle$, is also guaranteed to be constant in time, i.e.,

$$\langle\hat{H}^{(2)}\rangle = \langle\Psi(0)|\hat{H}^{(2)}|\Psi(0)\rangle \;\Rightarrow\; \frac{d}{dt}\langle\hat{H}^{(2)}\rangle = 0. \tag{3.171}$$

As expected, there is no such constraint for the mean value of the bare Hamiltonian of qubit (1), $\langle\hat{H}^{(1)}\rangle(t)$, and it is free to evolve in time. Notice that this conclusion is a very general statement and does not depend on our particular physical system. It is a simple consequence of the previous commutation relations[am]. Figure 2 illustrates this behaviour

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[al] It is worth mentioning this is a convenient simplifying hypothesis that does not limit the computational analysis or the conclusions.

[am] That is what happens in the usual dephasing model, for instance.

for the initially uncorrelated qubits: while $\langle \hat{H}^{(1)} \rangle(t)$ continuously oscillates in time, $\langle \hat{H}^{(2)} \rangle$ maintains its initially null value and keeps constant throughout the whole dynamics. This happens because the whole system's internal energy, $U^{(0)}$, is shared between the local bare Hamiltonians and the interaction term, such that

$$U^{(0)} = \langle \hat{H}^{(1)} \rangle(t) + \langle \hat{H}^{(2)} \rangle(t) + \langle \hat{H}_{int} \rangle(t). \tag{3.172}$$

Thus, if Eq. (3.171) above is satisfied and given that $\frac{d}{dt}U^{(0)} = 0$, we automatically have

$$\frac{d}{dt}\langle \hat{H}^{(1)} \rangle(t) = -\frac{d}{dt}\langle \hat{H}_{int} \rangle(t). \tag{3.173}$$

Along these lines, if the local internal energies are solely associated with the bare Hamiltonian's expectation values, $\langle \hat{H}^{(1,2)} \rangle(t)$, we would be led to conclude that only qubit (1) exchanges energy, even though both qubits continuously evolves in time. It would also imply that the interaction term - essentially - works as an energetic source/sink for this particular qubit since all the exchanges would be attributed only to the energy trapped within its expectation value.

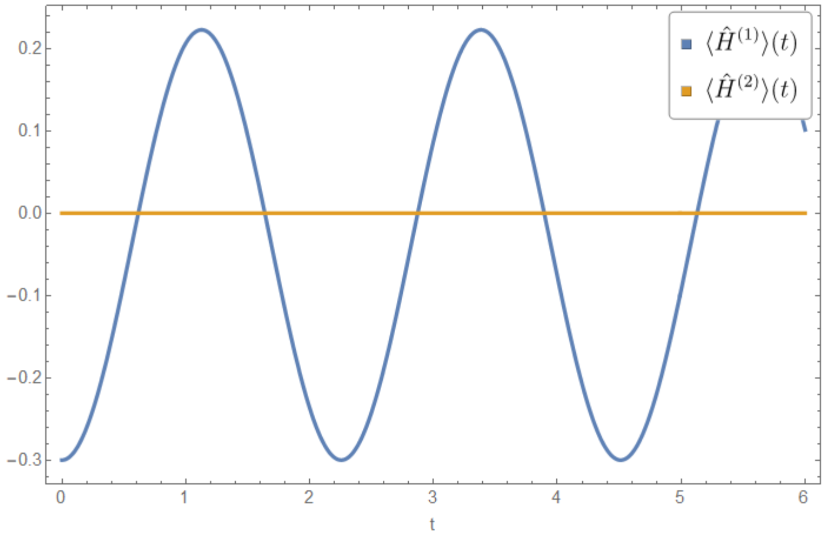
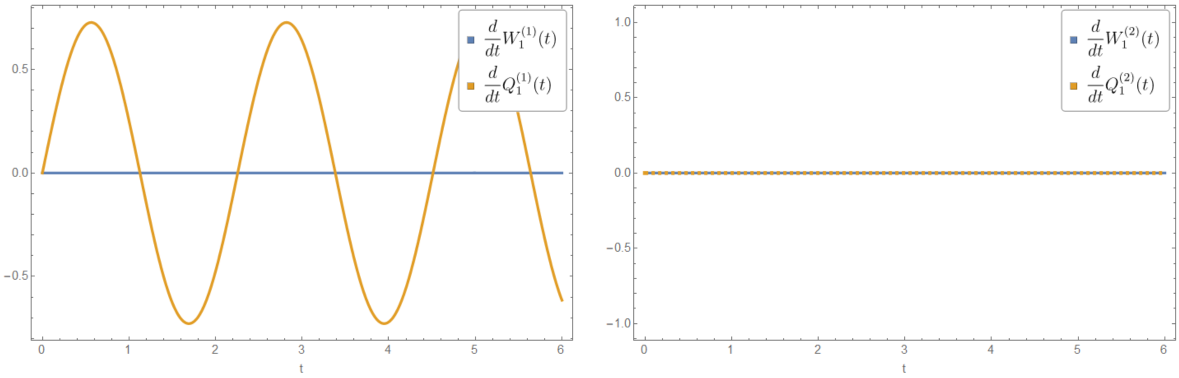


Figure 2 – Dynamical behaviour of the expectation values of the local bare Hamiltonians. On the one hand, since $[\hat{H}^{(2)}, \hat{H}_{int}] = 0$, the populations of $\hat{\rho}^{(2)}$ in the $\hat{H}^{(2)}$ basis are time-invariant and, therefore, $\frac{d}{dt}\langle \hat{H}^{(2)} \rangle(t) = 0$ for all t. On the other, $\frac{d}{dt}\langle \hat{H}^{(1)} \rangle(t) \neq 0$ and $\langle \hat{H}^{(1)} \rangle(t)$ continuously oscillates in time.

Source: By the author.

Besides, considering the discussions presented in Section (3.6.3.1.2), this simple example also provides an interesting scenario to analyze and compare the behaviours of potential definitions of quantum work and heat. In this sense, given Alicki's proposal, shown in Eqs. (3.142, 3.143), work is associated with changes in the local bare Hamiltonian, while heat is linked with the time evolution of the density matrix. Thus, according to these expressions, it is clear that both qubits do not perform work since $\frac{d}{dt}\hat{H}^{(1,2)} = 0$, which implies that the all energy exchange of qubit (1) with the interaction term is entirely interpreted as heat, while for qubit (2), this quantity is absent, i.e., $\frac{d}{dt}W_1^{(1,2)}(t) = 0$, $\frac{d}{dt}Q_1^{(1)}(t) = tr\left\{\hat{H}^{(1)}\frac{d}{dt}\hat{\rho}^{(1)}(t)\right\} = -\frac{d}{dt}\langle\hat{H}_{int}\rangle(t)$ and $\frac{d}{dt}Q_1^{(2)}(t) = 0$. Figure 3 reproduces the fluxes of Alicki's work and heat during the dynamics for both subsystems. Additionally, we might perform the same analyses for the work and heat forms depicted by Eqs. (3.146, 3.147), where work is related to modifications in the bare Hamiltonian spectrum while heat depends on the dynamics of both the density matrix and the bare Hamiltonian eigenstates. Nevertheless, since, by hypothesis, $\hat{H}^{(1,2)}$ are constant in time, we can show that these expressions and Alicki's proposal agree with each other for this particular scenario (see Eqs. (3.148, 3.149)), i.e., $Q_2^{(1,2)}(t) = Q_1^{(1,2)}(t)$ and $W_2^{(1,2)}(t) = W_1^{(1,2)}(t)$ for all t.



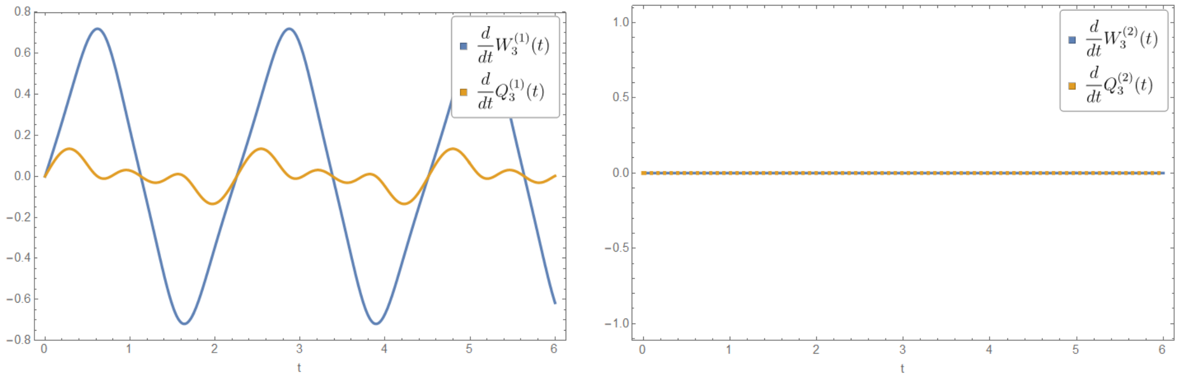
(a) Alicki's proposal for qubit (1)

(b) Alicki's proposal for qubit (2)

Figure 3 – According to Alicki's form of work and heat fluxes (see Eqs. (3.142,3.143)): **(a)** Qubit (1) does not perform work, and all energy exchange with the interaction term is interpreted as heat, i.e., $\frac{d}{dt}W_1^{(1,2)}(t) = 0$ and $\frac{d}{dt}Q_1^{(1)}(t) = -\frac{d}{dt}\langle\hat{H}_{int}\rangle(t)$; **(b)** The energy of qubit (2) is neither submitted to work-like nor heat-like energy changes.

Source: By the author.

Finally, we can also consider the expressions proposed by (214, 215) and shown in Eqs. (3.152, 3.153). According to this proposal, heat is bound to modifications in the populations of the density matrix, while work depends on the dynamics of both the local bare Hamiltonian and the instantaneous basis of $\hat{\rho}^{(1,2)}$, i.e., heat is directly associated with $\left\{\frac{d}{dt}\lambda_j^2(t)\right\}_j$ due to its relationship with $\frac{d}{dt}S_{vN}[\hat{\rho}^{(1,2)}(t)]$, and work is linked to the remaining terms $\left\{\frac{d}{dt}\left(\langle\varphi_j^{(1,2)}(t)|\hat{H}^{(1,2)}|\varphi_j^{(1,2)}(t)\rangle\right)\right\}_j$. Figure 4 shows the behaviour of the work and heat fluxes for both qubits. In comparison with the previous proposals, despite $\hat{H}^{(1)}$ being time-independent, part of the energy exchanged between qubit (1) and the interaction term is identified as work performed due to the dynamics of the basis $\{|\varphi_{1,2}^{(1)}(t)\rangle\}$, i.e., both work and heat are present such that $\frac{d}{dt}\langle\hat{H}^{(1)}\rangle(t) = \frac{d}{dt}W_3^{(1)}(t) + \frac{d}{dt}Q_3^{(1)}(t) = -\frac{d}{dt}\langle\hat{H}_{int}\rangle(t)$. Interestingly, for qubit (2), the structure of the dynamics guarantees neither work nor heat exchange during the interaction, $\frac{d}{dt}W_3^{(2)}(t) = \frac{d}{dt}Q_3^{(2)}(t) = 0$ for all t. It is worth emphasizing



(a) (214, 215) proposal for qubit (1) (b) (214, 215) proposal for qubit (2)

Figure 4 – According to Eqs. (3.152, 3.153): **(a)** The energetics between qubit (1) and the interaction term has separated contribution from both work and heat, i.e., $\frac{d}{dt}\langle\hat{H}^{(1)}\rangle(t) = \frac{d}{dt}W_3^{(1)}(t) + \frac{d}{dt}Q_3^{(1)}(t) = -\frac{d}{dt}\langle\hat{H}_{int}\rangle(t)$; **(b)** Qubit (2) neither performs work nor exchanges heat. Note this happens despite its dynamics and the clear oscillation of its von Neumann entropy $S_{vN}[\hat{\rho}^{(2)}(t)]$ (see Figure 1b).
Source: By the author.

that this occurs even though its von Neumann entropy $S_{vN}[\hat{\rho}^{(2)}(t)]$ oscillates in time (see Figure 1b), which is in clear contrast with the original thermodynamic motivation of associating heat with energy modification accompanied by entropic changes. This context is similar to the situation presented in. (216)

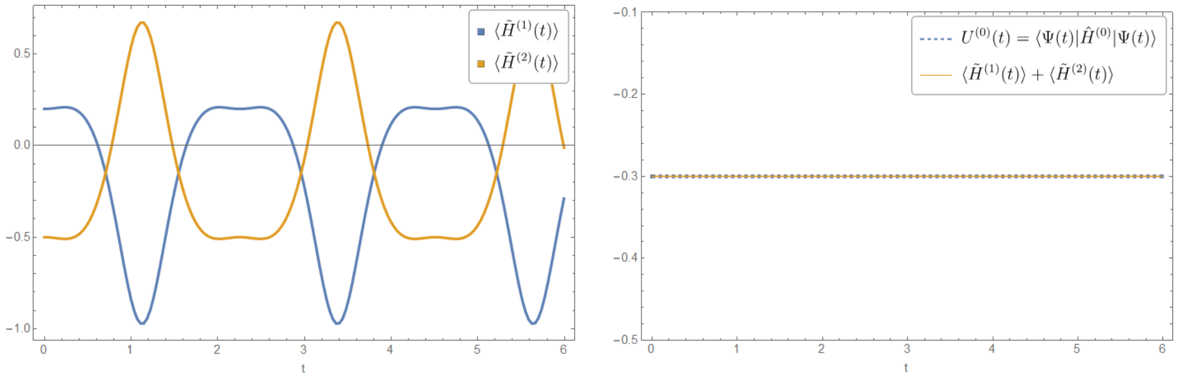
As we saw earlier, instead of focusing on the local bare Hamiltonians $\hat{H}^{(1,2)}$, if we use the local effective ones, $\tilde{H}^{(1,2)}(t)$, as the representative operators for quantifying local internal energies, the energy becomes additive and, therefore, the whole internal energy is simply written as

$$U^{(0)} = \langle\tilde{H}^{(1)}(t)\rangle + \langle\tilde{H}^{(2)}(t)\rangle. \tag{3.174}$$

According to this formulation, both qubits exchange energy continuously, such that

$$\frac{d}{dt}\langle\tilde{H}^{(1)}(t)\rangle = -\frac{d}{dt}\langle\tilde{H}^{(2)}(t)\rangle, \tag{3.175}$$

and there is no space for additional elements working as energetic sources or sinks, i.e., the qubits are the only entities required for characterizing the energetics within $|\Psi(t)\rangle$. The dynamics of the expectation values of the local effective Hamiltonians of our example are depicted in Figure 5a. Thus, it is clear that during the interaction, all energy flowing outside qubit (1) is entirely acquired by qubit (2) and vice versa. Besides, Figure 5b shows that the sum of both local quantities is constant and equal to the whole system's internal energy, which illustrates the additivity property presented in Eq. (3.174) above. Notice that, while the time-dependency of $\langle\hat{H}^{(1)}\rangle(t)$ is only due to the state $\hat{\rho}^{(1)}(t)$ dynamics, the $\tilde{H}^{(1,2)}(t)$ are explicitly time-dependent and play a significant role in the changes of their mean values $\langle\tilde{H}^{(1,2)}(t)\rangle$. In this sense, it is interesting to contrast the static nature of the bare Hamiltonians with the dynamic behaviour of the local effective operators. In order



(a) Local effective Hamiltonians

(b) Whole's internal energy

Figure 5 – Dynamical behaviour of the expectation values of the local effective Hamiltonians and its relationship with the whole's internal energy. **(a)** Interplay between $\langle\tilde{H}^{(1)}(t)\rangle$ and $\langle\tilde{H}^{(2)}(t)\rangle$. If $\tilde{H}^{(1,2)}(t)$ are interpreted as the representative operators for quantifying local internal energies, then all energy lost from qubit (1) is obtained by qubit (2), and vice versa; **(b)** The sum of the expectation values of the local effective Hamiltonians is equal to the whole's internal energy. This plot illustrates the energy additivity.

Source: By the author.

to do that, let us cast their following spectral decompositions

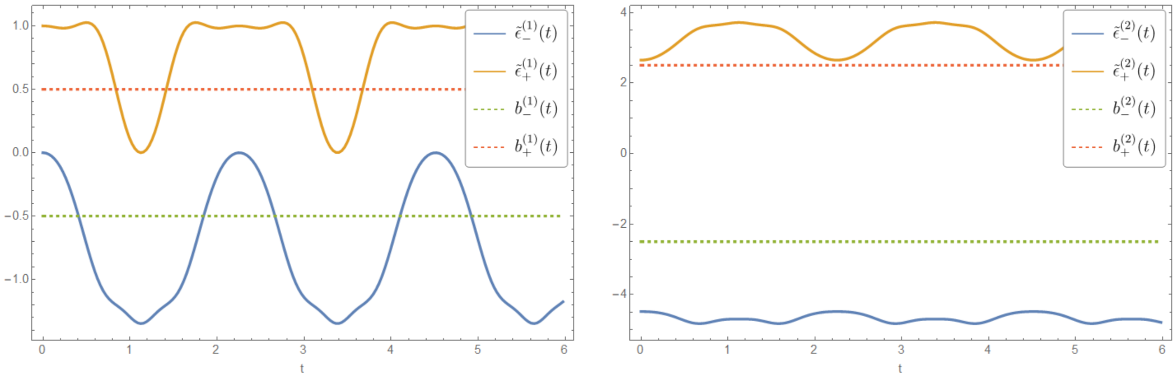
$$\hat{H}^{(1,2)} \equiv \sum_{j=\pm} b_j^{(1,2)} |b_j^{(1,2)}\rangle\langle b_j^{(1,2)}| \tag{3.176}$$

and

$$\tilde{H}^{(1,2)}(t) \equiv \sum_{j=\pm} \tilde{\epsilon}_j^{(1,2)}(t) |\tilde{\epsilon}_j^{(1,2)}(t)\rangle\langle\tilde{\epsilon}_j^{(1,2)}(t)| \tag{3.177}$$

where $\{b_\pm^{(1,2)} = \pm\hbar\frac{\omega_{1,2}}{2}\}$ and $\{\tilde{\epsilon}_\pm^{(1,2)}(t)\}$ are the respective eigenvalues of $\hat{H}^{(1,2)}$ and $\tilde{H}^{(1,2)}(t)$, while $\{|b_\pm^{(1)}\rangle = |\pm_z^{(1)}\rangle\}$, $\{|b_\pm^{(2)}\rangle = |\pm_y^{(2)}\rangle\}$ and $\{|\tilde{\epsilon}_\pm^{(1,2)}(t)\rangle\}$ are the eigenbasis of $\hat{H}^{(1)}$, $\hat{H}^{(2)}$ and $\tilde{H}^{(1,2)}(t)$, respectively. Figures 6a and 6b portray the dynamics of their energy levels. The time dependency of $\{\tilde{\epsilon}_\pm^{(1,2)}(t)\}$ is a direct consequence of the interaction term that is automatically comprised within the local effective operators (see Eq. (3.18)). Interestingly, not only these eigenvalues are time-dependent, but also the energy gaps are modulated in time. Given $\hbar\omega_{1,2} = b_+^{(1,2)} - b_-^{(1,2)}$ and $\hbar\tilde{\omega}_{1,2}(t) = \tilde{\epsilon}_+^{(1,2)}(t) - \tilde{\epsilon}_-^{(1,2)}(t)$, Figures 7a and 7b illustrate how the local gaps $\hbar\tilde{\omega}_{1,2}(t)$ change, while $\hbar\omega_{1,2}$ is maintained fixed during the whole dynamics.

Finally, as mentioned earlier, the use of the local effective Hamiltonians also provides an interesting starting point for discussing a general, exact and symmetrical understanding of quantum work and heat. Hence, let us compare the potential approaches for these quantities presented in Section (3.6.3.2). Along these lines, Eqs. (3.156, 3.157) are similar to Alicki's proposal. However, since the internal energy is computed by $\langle\tilde{H}^{(1,2)}(t)\rangle$, heat is associated with changes in the whole density matrix, and work is the energy exchange related to the local effective Hamiltonian dynamics. Thus, work is a direct outcome

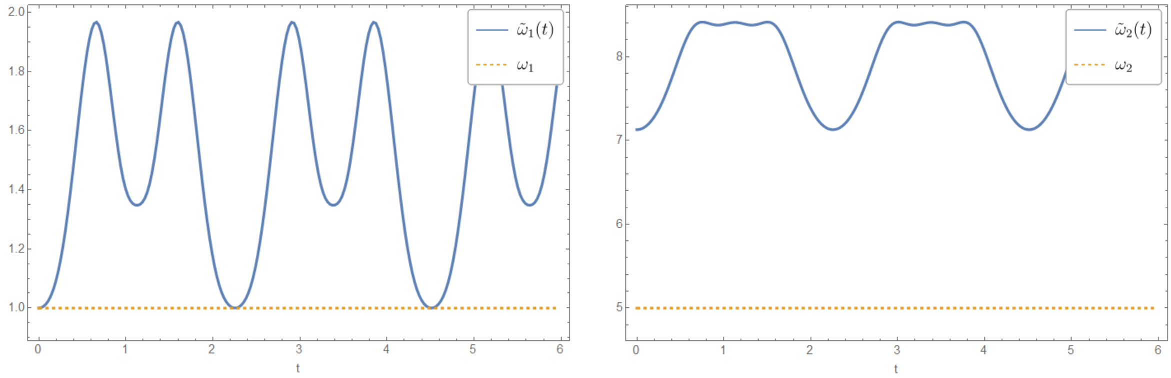


(a) Spectrum - Qubit (1)

(b) Spectrum - Qubit (2)

Figure 6 – Dynamical behaviour of the spectrum of the bare and local effective Hamiltonians, for both qubits. The bare eigenvalues $\{b_\pm^{(1,2)}\}$ are constant, while the local effective ones $\{\tilde{\epsilon}_\pm^{(1,2)}(t)\}$ clearly change in time. **(a)** Qubit (1); **(b)** Qubit (2).

Source: By the author.



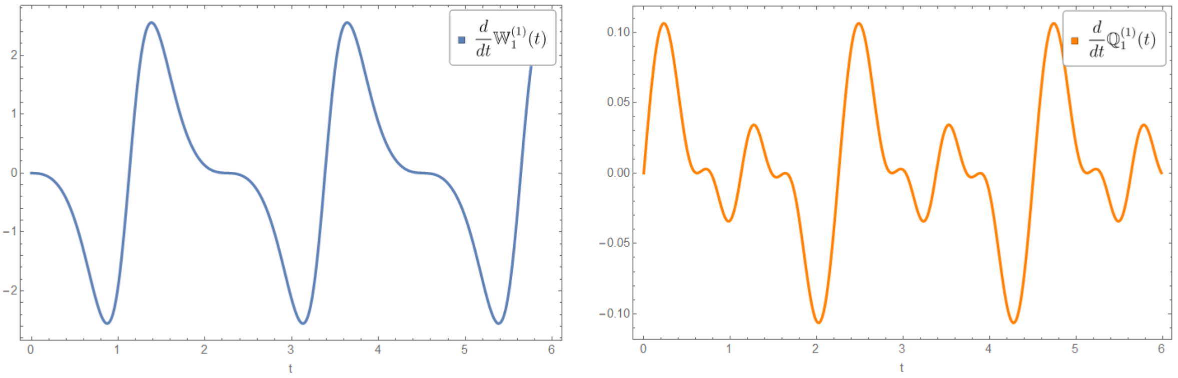
(a) Spectral gaps - Qubit (1)

(b) Spectral gaps - Qubit (2)

Figure 7 – Dynamical behaviour of the spectral gaps of the bare and local effective Hamiltonians, for both qubits. The changes in the spectrum modulate the local gaps $\tilde{\omega}_{1,2}(t) = \tilde{\epsilon}_+^{(1,2)}(t) - \tilde{\epsilon}_-^{(1,2)}(t)$ between the effective energy levels while $\hbar\omega_{1,2} = b_+^{(1,2)} - b_-^{(1,2)}$ is maintained fixed. **(a)** Qubit (1); **(b)** Qubit (2).

Source: By the author.

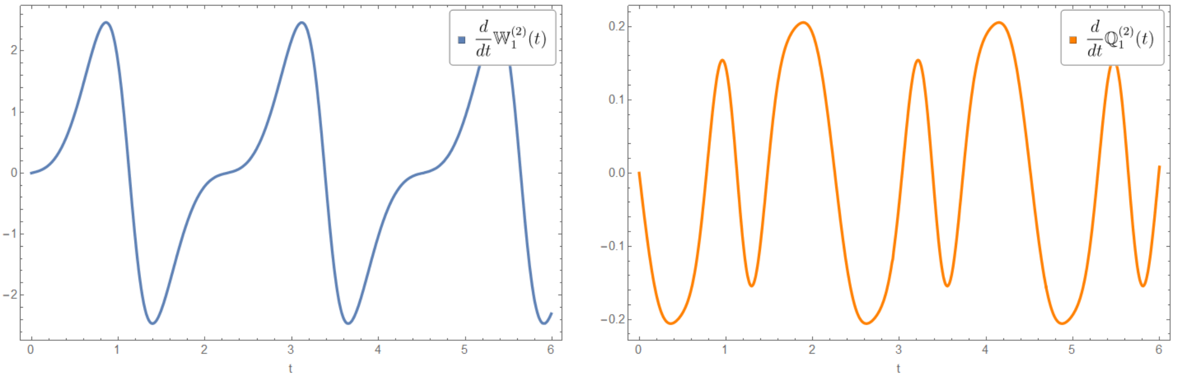
of the interactions between the qubits instead of being the result of the addition of classical external control. Figures 8 and 9 reproduce the non-null work and heat fluxes, $\frac{d}{dt}\mathbb{W}_1^{(1,2)}(t)$ and $\frac{d}{dt}\mathbb{Q}_1^{(1,2)}(t)$, during the dynamics for qubits (1) and (2), respectively. Additionally, Figure 10a shows the behaviour of the non-null net work and net heat fluxes involved during the process, where $\mathbb{W}_1(t) = \mathbb{W}_1^{(1)}(t) + \mathbb{W}_1^{(2)}(t)$ and $\mathbb{Q}_1(t) = \mathbb{Q}_1^{(1)}(t) + \mathbb{Q}_1^{(2)}(t)$, while Figure 10b confirms that all net energetic exchanges sum up to zero, i.e., $\frac{d}{dt}\mathbb{W}_1(t) + \frac{d}{dt}\mathbb{Q}_1(t) = 0$ (see Eq. (3.155)). It is worth mentioning that earlier was shown that the analogue forms of Eqs. (3.152, 3.153), considering the local effective Hamiltonians, are equivalent to the previous ones, i.e., $\mathbb{W}_1^{(1,2)}(t) = \mathbb{W}_3^{(1,2)}(t)$ and $\mathbb{Q}_1^{(1,2)}(t) = \mathbb{Q}_3^{(1,2)}(t)$.



(a) Alicki's form of work flux for qubit (1) (b) Alicki's form of heat flux for qubit (1)

Figure 8 – Work and heat fluxes according to Eqs. (3.156, 3.157) for qubit (1). **(a)** Work flux; **(b)** Heat flux.

Source: By the author.



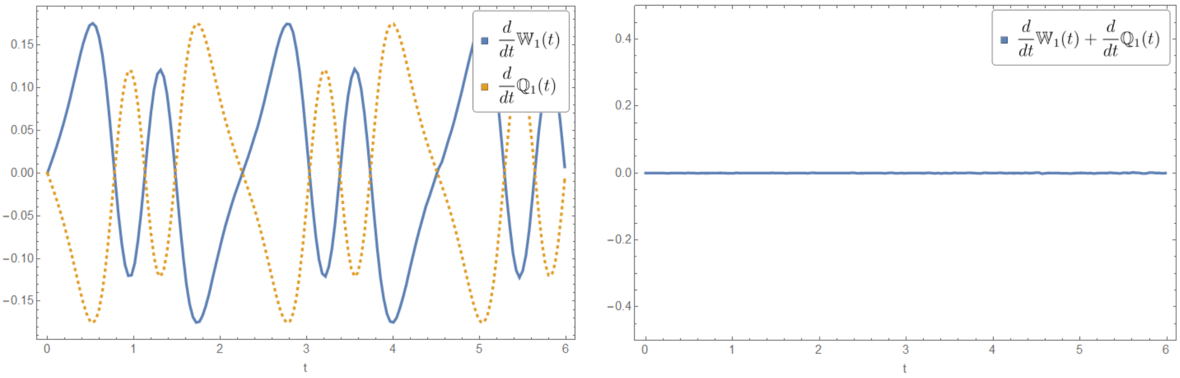
(a) Alicki's form of work flux for qubit (2) (b) Alicki's form of heat flux for qubit (2)

Figure 9 – Work and heat fluxes according to Eqs. (3.156, 3.157) for qubit (2). **(a)** Work flux; **(b)** Heat flux.

Source: By the author.

Alternatively, we might define these quantities according to Eqs. (3.163, 3.164). In this case, work is associated with changes in the local effective Hamiltonian spectrum, $\left\{\frac{d}{dt}\tilde{\epsilon}_j^{(1,2)}(t)\right\}_j$, and heat depends both on the dynamics of the density matrix $\hat{\rho}^{(1,2)}(t)$ and the basis $\left\{|\tilde{\epsilon}_j^{(1,2)}(t)\rangle\right\}$. Figures 11a and 11b show the interplay between work and heat fluxes, $\frac{d}{dt}\mathbb{W}_2^{(1,2)}(t)$ and $\frac{d}{dt}\mathbb{Q}_2^{(1,2)}(t)$, for qubit (1) and (2), respectively. Similarly to the previous proposal, Figure 12a presents the non-null dynamics of the net work and net heat fluxes during the interaction, where $\mathbb{W}_2(t) = \mathbb{W}_2^{(1)}(t) + \mathbb{W}_2^{(2)}(t)$ and $\mathbb{Q}_2(t) = \mathbb{Q}_2^{(1)}(t) + \mathbb{Q}_2^{(2)}(t)$. Besides, Figure 12b shows that all net energetic exchanges within the bipartition computed with these expressions are also in accordance with Eq. (3.155), i.e., they sum up to zero.

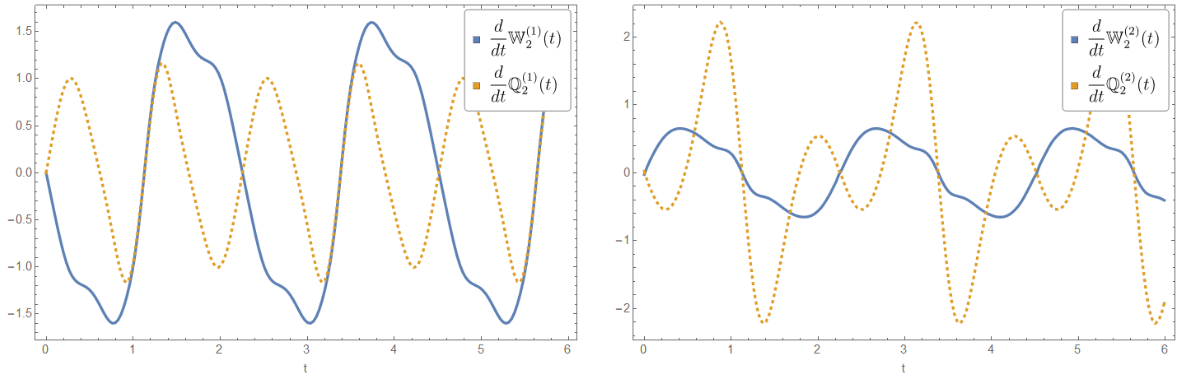
Therefore, it is clear that different work and heat proposals may represent radically distinct thermodynamic scenarios. Still, the use of $\tilde{H}^{(1,2)}(t)$ provides a consistent



(a) Net work and net heat fluxes

(b) Net energetic exchange

Figure 10 – Net energy fluxes according to Eqs. (3.156, 3.157). **(a)** The total work flux performed and the total heat flux transferred throughout the dynamics; **(b)** All net energetic exchanges involved during the whole system dynamics sum up to zero, Eq. (3.155).
Source: By the author.



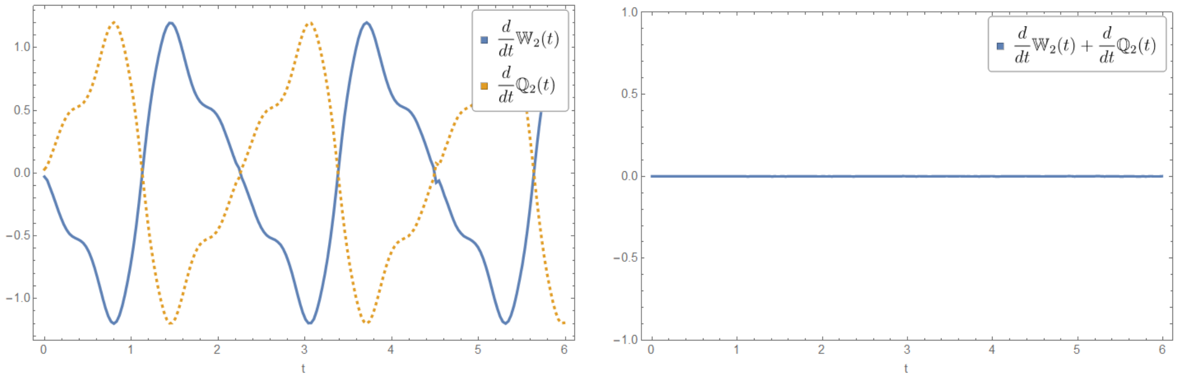
(a) Work and heat fluxes for qubit (1)

(b) Work and heat fluxes for qubit (2)

Figure 11 – Energy fluxes according to Eqs. (3.163, 3.164). **(a)** Qubit (1); **(b)** Qubit (2).
Source: By the author.

foundation for advancing such discussions in an absolutely general manner.

In short, it was both illustrated a simple example of the application of our local effective Hamiltonians formalism and highlighted a challenging issue of the usual identification of the bare Hamiltonians as the operators for representing the local internal energies whenever the interaction term $\hat{H}_{int}$ is non-negligible (and the strict energy conservation is not applicable). While the latter identification requires the interpretation of the interaction term as an additional energetic source or sink, the former only attributes local internal energies for the described subsystems. In this particular physical system, the global Hamiltonian structure guarantees that $\langle \hat{H}^{(2)} \rangle$ is a constant of motion, even though $\hat{\rho}^{(2)}(t)$ explicitly evolves in time (Figure 1), and the mean value $\langle \hat{H}^{(1)} \rangle$ changes (Figure 2). This behaviour, of course, reflects the non-additivity of the expectation values of the bare



(a) Net work and net heat fluxes

(b) Net energetic exchange

Figure 12 – Net energy fluxes according to Eqs. (3.163, 3.164). **(a)** The total work flux performed and the total heat flux transferred throughout the dynamics; **(b)** All net energetic exchanges involved during the whole system dynamics sum up to zero, Eq. (3.155).

Source: By the author.

Hamiltonians and the essential role played by the interaction in the total internal energy computation. Naturally, such a role is also critical for characterizing energy exchanges and must be appreciated, in one way or another, into any *consistent* and *general* definition of work and heat. Along these lines, since Alicki's definition proposal in (56), the bare Hamiltonians represent a common starting point for defining these thermodynamic quantities, even when considered alternative forms, such as the presented in. (214,215) In contrast, the use of the expectation values of the local effective Hamiltonians $\langle \tilde{H}^{(1,2)}(t)\rangle$ as the representative operators for characterizing physical internal energies satisfies the additivity property and offers an important interpretative advantage for the framework of quantum thermodynamics.

3.8 Generalization for mixed states

In this section, we will take our approach one step further by allowing the possibility of describing *mixed* quantum states. During the previous sections, we explicitly assumed a finite, isolated and nondegenerate pure quantum system, depicted by $|\Psi(t)\rangle\langle\Psi(t)|$, composed of two arbitrary smaller interacting subsystems, (1) and (2), with dimensions $d^{(k)} := dim(\mathcal{H}^{(k)})$, such that $d^{(0)} = (d^{(1)} + d^{(2)})$ and - without any loss of generality - $d^{(1)} \leq d^{(2)}$. The fully quantum autonomous object is described by the time-independent Hamiltonian $\hat{H}^{(0)}$ that generates the whole system dynamics, such that

$$\hat{H}^{(0)} = \hat{H}^{(1)} \otimes \hat{1}^{(2)} + \hat{1}^{(1)} \otimes \hat{H}^{(2)} + \hat{H}_{int}, \tag{3.178}$$

where $\hat{H}^{(1,2)} \in \mathcal{L}(\mathcal{H}^{(1,2)})$ are the local bare Hamiltonians of each subsystem and $\hat{H}_{int} \in \mathcal{L}(\mathcal{H}^{(0)})$ is the interaction between them. Let us now generalize and expand our formalism to include a more comprehensive and realistic experimental description[an]. From a pragmatical point of view, this setting only characterizes specific situations. In real-world scenarios, the quantum system must be somehow experimentally prepared, in a way that it is inevitably distributed across an ensemble of possible states. This, of course, corresponds to a classical lack of information due to the preparation procedure itself. In these cases, the system in question is better described by a statistical mixture of pure states $\{P_\eta, |\Psi_\eta(t)\rangle \in \mathcal{H}^{(0)} = \mathcal{H}^{(1)} \otimes \mathcal{H}^{(2)}\}_{\eta=1,\dots,d^{(0)}}$, such that

$$\hat{\rho}^{(0)}(t) \equiv \sum_{\eta=1}^{d^{(0)}} P_\eta \hat{\sigma}_\eta^{(0)}(t), \tag{3.179}$$

where $\{\hat{\sigma}_\eta^{(0)}(t) \equiv |\Psi_\eta(t)\rangle\langle\Psi_\eta(t)|\}_\eta$ are pure states, $\langle\Psi_\alpha(t)|\Psi_\beta(t)\rangle = \delta_{\alpha\beta}$ and $tr\{\hat{\rho}^{(0)}(t)\} = \sum_{\eta=1}^{d^{(0)}} P_\eta = 1$. Note that such description also provides us with the means to represent and characterize systems initially prepared at thermal states, i.e., if $\hat{H}^{(0)} \equiv \sum_{\eta=1}^{d^{(0)}} b_\eta^{(0)} |b_\eta^{(0)}\rangle\langle b_\eta^{(0)}|$, then $P_\eta \equiv \frac{e^{-\beta b_\eta^{(0)}}}{Z^{(0)}}$ and $|\Psi_\eta(t_0)\rangle \equiv |b_\eta^{(0)}\rangle$ in a way that $\hat{\rho}^{(0)}(t_0) = \sum_{\eta=1}^{d^{(0)}} \frac{e^{-\beta b_\eta^{(0)}}}{Z^{(0)}} |b_\eta^{(0)}\rangle\langle b_\eta^{(0)}|$. Also, since the whole system is isolated, the populations $\{P_\eta\}_\eta$ remains constant throughout the unitary dynamics. Thus, it is clear that a single pure state, instead of the convex sum above, is just a particular case of a much more broad representation, where $P_\eta = \delta_{0\eta}$ and $\hat{\rho}^{(0)}(t) = \hat{\sigma}_0^{(0)}(t)$. Locally, as will be shown below, such a mixed state implies that both subsystems will also be portrayed as ensembles themselves, although not of pure states. It is worth mentioning that one may argue that there is a clear and noticeable ambiguity in such a process: it is well-known that there are infinite possible ways to express the same density matrix $\hat{\rho}^{(0)}(t)$ as a convex sum of pure - and not necessarily orthogonal - states. However, on the one hand, from a physical perspective, all possible representations are indistinguishable, thus any observable or internal thermodynamic description should not depend on this choice. On the other, there is a unique description in terms of an orthonormal basis which is given by the spectral decomposition above. Thus, Eq. (3.179) represents the most natural depiction choice for our purposes. Finally, from now on, the addition of a label η will be necessary to identify which element of Eq. (3.179) we are dealing with and to distinguish an ensemble or a pure-state-level treatment.

Now, let us proceed in complete analogy with what was previously shown in Section (3.1). Every pure state dynamics is governed by the usual Schrödinger equation $i\hbar\frac{d}{dt}|\Psi_\eta(t)\rangle = \hat{H}^{(0)}|\Psi_\eta(t)\rangle$, such that for any initial state $|\Psi_\eta(t_0)\rangle$ and $t \geq t_0$ we have

$$|\Psi_\eta(t)\rangle = \hat{\mathcal{U}}(t,t_0)|\Psi_\eta(t_0)\rangle, \tag{3.180}$$

where $\hat{\mathcal{U}}(t,t_0) = e^{-\frac{i}{\hbar}\hat{H}^{(0)}(t-t_0)} \in \mathcal{L}(\mathcal{H}^{(0)})$ is the time-evolution operator of the whole bipartite system. Then, let us represent them according to their respective Schmidt decompo-

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[an] Many of the steps presented here - from now on - will be very similar to those shown in Section (3.1). For completeness and for establishing the new notation, the essential features will be repeated. However, to avoid redundancy, some discussions will be purposely suppressed.

sition form

$$|\Psi_\eta(t)\rangle = \sum_{j=1}^{d^{(1)}} \lambda_{\eta j}(t)|\varphi^{(1)}_{\eta j}(t)\rangle \otimes |\varphi^{(2)}_{\eta j}(t)\rangle, \tag{3.181}$$

for every time t, where $\{\lambda_{\eta j}(t) \geq 0\}_j$ and $\{|\varphi^{(k)}_{\eta j}(t)\rangle\}_j \in \mathcal{H}^{(k)}$ are the ηth time-local Schmidt coefficients and local Schmidt basis of subsystem (k), respectively. The pure states $\{|\Psi_\eta(t)\rangle\}_\eta$ orthonormality implies that $\sum_{q,j=1}^{d^{(1)}} \lambda_{\beta j}(t)\lambda_{\alpha q}(t)\langle\varphi^{(1)}_{\alpha q}(t)|\varphi^{(1)}_{\beta j}(t)\rangle\langle\varphi^{(2)}_{\alpha q}(t)|\varphi^{(2)}_{\beta j}(t)\rangle = \delta_{\alpha\beta}$ and, therefore, the normalization $\sum_{j=1}^{d^{(1)}} \lambda^2_{\eta j}(t) = 1$ for all η, also the orthonormality of the local basis elements assure that $\langle\varphi^{(k)}_{\eta\alpha}(t)|\varphi^{(l)}_{\eta\beta}(t)\rangle = \delta_{kl}\delta_{\alpha\beta}$. Besides, since each ηth set $\{|\varphi^{(k)}_{\eta j}(t)\rangle\}_j$ constitute a possible basis for the same Hilbert space $\mathcal{H}^{(k)}$, any pair of Schmidt basis for a given subsystem should be unitarily related, such that

$$|\varphi^{(k)}_{\eta j}(t)\rangle = \hat{T}^{(k)}_{\eta\alpha}(t)|\varphi^{(k)}_{\alpha j}(t)\rangle, \tag{3.182}$$

where $\hat{T}^{(k)}_{\eta\alpha}(t) = \sum_{m=1}^{d^{(k)}} |\varphi^{(k)}_{\eta m}(t)\rangle\langle\varphi^{(k)}_{\alpha m}(t)|$, $\hat{T}^{(k)}_{\alpha\eta}(t) = \hat{T}^{(k)\dagger}_{\eta\alpha}(t)$ and $\hat{T}^{(k)}_{\eta\alpha}(t)\hat{T}^{(k)\dagger}_{\eta\alpha}(t) = \hat{1}^{(k)}$.

Concerning the subsystems representations, for each possible pure state $|\Psi_\eta(t)\rangle$ of the whole, one can find the local states by the usual procedure of partial tracing their complementary degrees of freedom, such that $\hat{\sigma}^{(1,2)}_\eta(t) \equiv tr_{2,1}\{\hat{\sigma}^{(0)}_\eta(t)\}$. Thus, as expected,

$$\hat{\sigma}^{(1)}_\eta(t) = \sum_{j=1}^{d^{(1)}} \lambda^2_{\eta j}(t)|\varphi^{(1)}_{\eta j}(t)\rangle\langle\varphi^{(1)}_{\eta j}(t)|, \tag{3.183}$$

$$\hat{\sigma}^{(2)}_\eta(t) = \sum_{j=1}^{d^{(1)}} \lambda^2_{\eta j}(t)|\varphi^{(2)}_{\eta j}(t)\rangle\langle\varphi^{(2)}_{\eta j}(t)|, \tag{3.184}$$

where the eigenvalues and eigenvectors are given by the Schmidt coefficients squared $\{\lambda^2_{\eta j}(t)\}_j$ and Schmidt basis $\{|\varphi^{(1,2)}_{\eta j}(t)\rangle\}_j$, respectively. Notice that Eqs. (3.183, 3.184) above do not describe the total local states, in the sense that they only represent the possible local density operators obtained from the whole distribution of pure states $\{P_\eta, |\Psi_\eta(t)\rangle\}_\eta$. This also characterizes a *subensemble* of local representations $\{P_\eta, \hat{\sigma}^{(1,2)}_\eta(t)\}_\eta$, such that the total local states are simply given by the averages

$$\hat{\rho}^{(1)}(t) \equiv tr_2\{\hat{\rho}^{(0)}(t)\} = \sum_{\eta=1}^{d^{(0)}} P_\eta \hat{\sigma}^{(1)}_\eta(t), \tag{3.185}$$

$$\hat{\rho}^{(2)}(t) \equiv tr_1\{\hat{\rho}^{(0)}(t)\} = \sum_{\eta=1}^{d^{(0)}} P_\eta \hat{\sigma}^{(2)}_\eta(t). \tag{3.186}$$

In short, every possible pure bipartite state from the mixed ensemble presented in Eq. (3.179), give rise to a pair of local density matrices $\hat{\sigma}^{(1,2)}_\eta(t)$ in such a way that the entire local states are given by the distribution portrayed in Eqs. (3.185, 3.186) above.

3.8.1 Schmidt basis dynamics and local effective Hamiltonians

Next, following the same reasoning used in Section (3.2), we are interested in a local dynamical description for the set of Schmidt basis $\{|\varphi^{(1,2)}_{\eta j}(t)\rangle\}_{\eta,j}$. At any time interval

$[t_0, t_1]$, instead of having a single curve associated with the whole system time-evolution, now we have an ensemble of possible trajectories $\{\mathcal{P}^{(0)}_\eta : |\Psi_\eta(t)\rangle,\ t \in [t_0, t_1]\}_\eta$ in the total Hilbert space $\mathcal{H}^{(0)}$. Thus, just like before, each path can be mapped into two coupled trajectories $\mathcal{P}^{(1,2)}_{\eta j} : |\varphi^{(1,2)}_{\eta j}(t)\rangle$, $t \in [t_0, t_1]$ followed by the Schmidt basis in their own Hilbert spaces $\mathcal{H}^{(1,2)}$, and the paths of the Schmidt coefficients, $\mathcal{P}^{\lambda}_{\eta j} : \lambda_{\eta j}(t) \geq 0,\ t \in [t_0, t_1]$, such that $\lambda^2_{\eta j}(t) \in [0, 1]$ for all j and η, and $\sum_{j=1}^{d^{(1)}} \lambda^2_{\eta j}(t) = 1$. Clearly, the whole time-evolution is fully characterized by the initial states $\{|\Psi_\eta(t_0)\rangle\}_\eta$ and the unitary operator $\hat{\mathcal{U}}(t, t_0)$ through Eq. (3.180), i.e., every possible initial condition will be time-evolved under the same generator. Nevertheless, the local dynamical behaviours will definitely depend on the whole pure state in question.

Let us define the local dynamical maps $\tilde{\mathcal{U}}^{(k)}_\eta : \mathcal{H}^{(k)} \to \mathcal{H}^{(k)}$ $(k = 1, 2)$ associated with the time-evolution of each ηth path from $\{\mathcal{P}^{(k)}_{\eta j}\}_j$, in a way that every Schmidt basis ket continuously follows

$$|\varphi^{(k)}_{\eta j}(t)\rangle = \tilde{\mathcal{U}}^{(k)}_\eta(t, t_0)|\varphi^{(k)}_{\eta j}(t_0)\rangle, \tag{3.187}$$

for any $t \geq t_0$, with $\underset{t\to t_0}{lim}|\varphi^{(k)}_{\eta j}(t)\rangle = |\varphi^{(k)}_{\eta j}(t_0)\rangle$ or $\underset{t\to t_0}{lim}\tilde{\mathcal{U}}^{(k)}_\eta(t, t_0) = \hat{1}^{(k)}$. This time-evolution operator is unitary, $\tilde{\mathcal{U}}^{(k)\dagger}_\eta(t, t_0)\tilde{\mathcal{U}}^{(k)}_\eta(t, t_0) = \hat{1}^{(k)}$, and should satisfy[ao]

$$i\hbar\frac{d}{dt}\tilde{\mathcal{U}}^{(k)}_\eta(t, t_0) = \tilde{H}^{(k)}_\eta(t)\tilde{\mathcal{U}}^{(k)}_\eta(t, t_0), \tag{3.188}$$

where $\tilde{H}^{(k)}_\eta(t) = \tilde{H}^{(k)\dagger}_\eta(t) \in \mathcal{L}(\mathcal{H}^{(k)})$ is a hermitian and possibly time-dependent operator. Then, from Eqs. (3.187, 3.188) we have

$$i\hbar\frac{d}{dt}|\varphi^{(k)}_{\eta j}(t)\rangle = \tilde{H}^{(k)}_\eta(t)|\varphi^{(k)}_{\eta j}(t)\rangle, \tag{3.189}$$

for all j and η. It is clear that $\tilde{H}^{(k)}_\eta(t)$ is the time-translation generator of the Schmidt basis $\{|\varphi^{(k)}_{\eta j}(t)\rangle\}_{\eta,j}$ and the ηth local effective Hamiltonian for subsystem (k) linked with the state $\hat{\sigma}^{(k)}_\eta(t)$. As before, this operator can be simply cast as

$$\tilde{H}^{(k)}_\eta(t) \equiv i\hbar\sum_{j=1}^{d^{(k)}}\frac{d}{dt}|\varphi^{(k)}_{\eta j}(t)\rangle\langle\varphi^{(k)}_{\eta j}(t)|. \tag{3.190}$$

Thus, essentially, we have a collection of local operators $\{\tilde{H}^{(k)}_\eta(t)\}_\eta$ associated with the subensemble of local states $\{\hat{\sigma}^{(k)}_\eta(t)\}_\eta$. Interestingly, from Eq. (3.182), one can also show that all possible local effective Hamiltonians can be directly related as follows

$$\tilde{H}^{(k)}_\eta(t) = \hat{T}_{\eta\alpha}(t)\tilde{H}^{(k)}_\alpha(t)\hat{T}^{(k)\dagger}_{\eta\alpha}(t) - i\hbar\hat{T}_{\eta\alpha}(t)\frac{d}{dt}\hat{T}^{(k)\dagger}_{\eta\alpha}(t). \tag{3.191}$$

Also, for every η, one can break down Eq. (3.190) into the contributions of the local bare Hamiltonian $\hat{H}^{(k)}$ and the by-products of the interaction term $\hat{H}_{int}$. Using the spectral

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[ao] See Section (3.2) for more details.

decomposition from Eq. (3.15) and defining the projection $\langle b_j^{(k)}|\varphi_{\eta l}^{(k)}(t)\rangle := r_{j\eta l}^{(k)}(t)e^{-\frac{i}{\hbar}b_j^{(k)}t}$, one can rewrite the local effective Hamiltonians as

$$\tilde{H}_\eta^{(k)}(t) = \hat{H}^{(k)} + \hat{H}_{LS;\eta}^{(k)}(t) + \hat{H}_{X;\eta}^{(k)}(t), \tag{3.192}$$

where

$$\hat{H}_{LS;\eta}^{(k)}(t) := i\hbar\sum_{j=1}^{d^{(k)}}\left(\sum_{l=1}^{d^{(k)}}\frac{d}{dt}r_{j\eta l}^{(k)}(t)r_{j\eta l}^{(k)*}(t)\right)|b_j^{(k)}\rangle\langle b_j^{(k)}|, \tag{3.193}$$

$$\hat{H}_{X;\eta}^{(k)}(t) := i\hbar\sum_{j=1}^{d^{(k)}}\sum_{m\neq j}^{d^{(k)}}\left(\sum_{l=1}^{d^{(k)}}\frac{d}{dt}r_{m\eta l}^{(k)}(t)r_{j\eta l}^{(k)*}(t)\right)e^{\frac{i}{\hbar}\left(b_j^{(k)}-b_m^{(k)}\right)t}|b_m^{(k)}\rangle\langle b_j^{(k)}|. \tag{3.194}$$

Obviously, these expressions above have the same structure as the ones previously discussed. However, it is worth mentioning again that the local Hamiltonian time-dependency is induced by $\hat{H}_{LS;\eta}^{(k)}(t)$ and $\hat{H}_{X;\eta}^{(k)}(t)$, where the former is a general Lamb-shift-like term such that $[\hat{H}_{LS:\eta}^{(k)}(t), \hat{H}^{(k)}] = 0$ for all t and η, and the latter contain only non-diagonal elements in the bare Hamiltonian basis $\{|b_j^{(k)}\rangle\}_j$.

3.8.2 Local states dynamics

Although mixed, the whole bipartite system is still assumed to be isolated. Thus, its dynamic is unitary and expressed by the usual Liouville-von Neumann equation below

$$i\hbar\frac{d}{dt}\hat{\rho}^{(0)}(t) = [\hat{H}^{(0)}, \hat{\rho}^{(0)}(t)], \tag{3.195}$$

which also implies - as already mentioned - that every pure state from the ensemble evolves unitarily (Eq. (3.180)) and $\frac{d}{dt}P_\eta = 0$ for all η. Locally, the subsystem's dynamics is not unitary and can be simply obtained by partial tracing the equation above, such that

$$i\hbar\frac{d}{dt}\hat{\rho}^{(k)}(t) = [\hat{H}^{(k)}, \hat{\rho}^{(k)}(t)] + tr_{\bar{k}}\{[\hat{H}_{int}, \hat{\rho}^{(0)}(t)]\}. \tag{3.196}$$

where it clearly depends on unitary and non-unitary parts. Nevertheless, given Eqs. (3.179, 3.185, 3.186) we might write similar expressions for each element of the local subensembles $\{\hat{\sigma}_\eta^{(k)}(t)\}_\eta$, i.e.,

$$i\hbar\frac{d}{dt}\hat{\sigma}_\eta^{(k)}(t) = [\hat{H}^{(k)}, \hat{\sigma}_\eta^{(k)}(t)] + tr_{\bar{k}}\{[\hat{H}_{int}, \hat{\sigma}_\eta^{(0)}(t)]\}, \tag{3.197}$$

which is similar to Eq. (3.27). Instead, the expression above might be analogously written as Eq. (3.28), such that

$$i\hbar\frac{d}{dt}\hat{\sigma}_\eta^{(k)}(t) = [\tilde{H}_\eta^{(k)}(t), \hat{\sigma}_\eta^{(k)}(t)] + i\hbar\sum_{j=1}^{d^{(1)}}\frac{d}{dt}\lambda_{\eta j}^2(t)|\varphi_{\eta j}^{(k)}(t)\rangle\langle\varphi_{\eta j}^{(k)}(t)|, \tag{3.198}$$

where the commutator is the unitary part, in terms of the effective Hamiltonian - instead of the bare one - and the remaining element is the non-unitary contribution represented by the population changes. Along these lines, now, there is a set of parametric curves

$\{\mathcal{C}_\eta^{(k)} : \hat{\sigma}_\eta^{(k)}(t), t \in [t_0, t_1]\}_\eta$ followed by the subsystem (k) in its respective density operator space $\mathscr{D}(\mathcal{H}^{(k)})$, where the unitary contribution is due to the generators of the Schmidt basis paths $\{\mathcal{P}_{\eta j}^{(k)}\}_{\eta,j}$, and the non-unitary factor is given by the population's trajectories $\{\mathcal{P}_{\eta j}^{(\lambda)}\}_{\eta,j}$.

Finally, since both Eq. (3.197) and Eq. (3.198) describe the same dynamics, it is clear that they must be directly associated. Hence, given Eq. (3.192), both unitary contributions satisfy the following equality

$$[\tilde{H}_\eta^{(k)}(t), \hat{\sigma}_\eta^{(k)}(t)] = [\hat{H}^{(k)}, \hat{\sigma}_\eta^{(k)}(t)] + [\hat{H}_{LS;\eta}^{(k)}(t), \hat{\sigma}_\eta^{(k)}(t)] + [\hat{H}_{X;\eta}^{(k)}(t), \hat{\sigma}_\eta^{(k)}(t)] \tag{3.199}$$

and, therefore,

$$tr_{\bar{k}}\{[\hat{H}_{int}, \hat{\sigma}_\eta^{(0)}(t)]\} = i\hbar \sum_{j=1}^{d^{(1)}} \frac{d}{dt}\lambda_{\eta j}^2(t)|\varphi_{\eta j}^{(k)}(t)\rangle\langle\varphi_{\eta j}^{(k)}(t)| + [\hat{H}_{LS;\eta}^{(k)}(t) + \hat{H}_{X;\eta}^{(k)}(t), \hat{\sigma}_\eta^{(k)}(t)], \tag{3.200}$$

for all η.

3.8.3 Local effective internal energy

Let us now characterize the energetics within this mixed bipartite quantum system. The whole system is isolated by hypothesis, thus it does not interact with any other element, classical or quantum. From an energetic point of view, it means the energy must be conserved inside the bipartition. Along these lines, the role of total internal energy is naturally - and unambiguously - attributed to the expectation value of the Hamiltonian $\hat{H}^{(0)}$, i.e.,

$$U^{(0)} \equiv \langle \hat{H}^{(0)} \rangle = tr\{\hat{H}^{(0)}\hat{\rho}^{(0)}(t)\}. \tag{3.201}$$

As expected, the unitary time evolution of $\hat{\rho}^{(0)}(t)$ automatically guarantees that this internal energy is a conserved quantity, such that

$$\frac{d}{dt}U^{(0)} = 0. \tag{3.202}$$

Additionally, given that the whole state is mixed, as shown in Eq. (3.179), one can easily cast the expectation value above as the following average over the ensemble of pure states

$$U^{(0)} = \sum_{\eta=1}^{d^{(0)}} P_\eta U_\eta^{(0)}, \tag{3.203}$$

where

$$U_\eta^{(0)} \equiv tr\{\hat{H}^{(0)}\hat{\sigma}_\eta^{(0)}(t)\} = \langle\Psi_\eta(t)|\hat{H}^{(0)}|\Psi_\eta(t)\rangle \tag{3.204}$$

is immediately recognized as the whole's internal energy relative to the ηth individual state $\hat{\sigma}_\eta^{(0)}(t)$, which also satisfy

$$\frac{d}{dt}U_\eta^{(0)} = 0 \tag{3.205}$$

for all η.

Nevertheless, we are interested to understand how exactly the internal energy is distributed between the bipartition. In this sense, it is clear that we can refer to and analyse the whole's internal energy both from the ensemble ($U^{(0)}$) and pure state ($U_\eta^{(0)}$) perspectives:

3.8.3.1 Pure state level

As discussed earlier, the direct use of the local bare Hamiltonians $\hat{H}^{(1,2)}$ as the proper operators for this task is not satisfactory for general scenarios. Thus, following the exact same procedure from Subsection (3.4.1.1), we will recognize the local effective Hamiltonians, $\tilde{H}_\eta^{(1,2)}(t)$, as the representative local operators for characterizing the physical internal energy of each possible pure state of the whole. Along these lines, since $\sum_{j=1}^{d^{(1)}} \lambda_{\eta j}^2(t) = 1$ and $\sum_{j=1}^{d^{(1)}} \lambda_{\eta j}(t) \frac{d}{dt} \lambda_{\eta j}(t) = \frac{1}{2} \frac{d}{dt} \sum_{j=1}^{d^{(1)}} \lambda_{\eta j}^2(t)$, we can show that

$$\langle \Psi_\eta(t) | \hat{H}^{(0)} | \Psi_\eta(t) \rangle = \langle \Psi_\eta(t) | \tilde{H}_\eta^{(1)}(t) | \Psi_\eta(t) \rangle + \langle \Psi_\eta(t) | \tilde{H}_\eta^{(2)}(t) | \Psi_\eta(t) \rangle \tag{3.206}$$

for every η, where $\langle \Psi_\eta(t) | \tilde{H}_\eta^{(1,2)}(t) | \Psi_\eta(t) \rangle = tr\{\tilde{H}_\eta^{(1,2)}(t) \hat{\sigma}_\eta^{(0)}(t)\} = tr_{1,2}\{\tilde{H}_\eta^{(1,2)}(t) \hat{\sigma}_\eta^{(1,2)}(t)\}$ is the expectation value of the local effective Hamiltonian concerning the ηth pure state. Hence, as long we identify

$$U_\eta^{(1,2)}(t) \equiv \langle \Psi_\eta(t) | \tilde{H}_\eta^{(1,2)}(t) | \Psi_\eta(t) \rangle \tag{3.207}$$

as the proper local effective internal energy of subsystem $(1,2)$, every possible element of the mixed ensemble $\hat{\rho}^{(0)}(t)$ will individually satisfy the energy additivity, such that

$$U_\eta^{(0)} = U_\eta^{(1)}(t) + U_\eta^{(2)}(t). \tag{3.208}$$

Besides, given the energy conservation property (Eq. (3.205)), the equation above also implies that the energy flowing from one subsystem is entirely obtained by the other, i.e.,

$$\frac{d}{dt} U_\eta^{(1)}(t) = -\frac{d}{dt} U_\eta^{(2)}(t). \tag{3.209}$$

Also, since $\hat{H}^{(0)} = \hat{H}^{(1)} \otimes \hat{1}^{(2)} + \hat{1}^{(1)} \otimes \hat{H}^{(2)} + \hat{H}_{int}$ and Eq. (3.206), it is straightforward to show that

$$\langle \Psi_\eta(t) | \hat{H}_{int} | \Psi_\eta(t) \rangle = \sum_{k=1,2} \langle \Psi_\eta(t) | \left(\hat{H}_{LS;\eta}^{(k)}(t) + \hat{H}_{X;\eta}^{(k)}(t) \right) | \Psi_\eta(t) \rangle. \tag{3.210}$$

3.8.3.2 Ensemble level

However, from the total ensemble perspective, the whole's internal energy is characterized by Eq. (3.203). Thus, along with Eq. (3.208), we obtain

$$U^{(0)} = U^{(1)}(t) + U^{(2)}(t), \tag{3.211}$$

where the entire local internal energies $U^{(1,2)}(t)$ are simply identified as the averages of its possible values

$$U^{(1,2)}(t) \equiv \sum_{\eta=1}^{d^{(0)}} P_\eta U_\eta^{(1,2)}(t), \tag{3.212}$$

which is clearly an additive property, such that

$$\frac{d}{dt}U^{(1)}(t) = -\frac{d}{dt}U^{(2)}(t). \tag{3.213}$$

As expected, these quantities automatically contain both the bare and interaction contributions, i.e.,

$$U^{(k)}(t) = \langle \hat{H}^{(k)} \rangle(t) + \sum_{\eta=1}^{d^{(0)}} P_\eta tr_k\{(\hat{H}_{LS;\eta}^{(k)}(t) + \hat{H}_{X;\eta}^{(k)}(t))\hat{\sigma}_\eta^{(k)}(t)\} \tag{3.214}$$

where $\langle \hat{H}^{(k)} \rangle(t) = tr_k\{\hat{H}^{(k)}\hat{\rho}^{(k)}(t)\}$. Additionally, one can generalize Eq. (3.210) and associate the expectation value of the interaction term, $\langle \hat{H}_{int} \rangle(t) \equiv tr\{\hat{H}_{int}\hat{\rho}^{(0)}(t)\}$, with the local operators $\hat{H}_{LS;\eta}^{(1,2)}(t)$ and $\hat{H}_{X;\eta}^{(1,2)}(t)$, such that

$$\langle \hat{H}_{int} \rangle(t) = \sum_{\eta=1}^{d^{(0)}} P_\eta \sum_{k=1,2} \langle \Psi_\eta(t)| \left(\hat{H}_{LS;\eta}^{(k)}(t) + \hat{H}_{X;\eta}^{(k)}(t)\right) |\Psi_\eta(t)\rangle. \tag{3.215}$$

Notice that the entire local internal energies $U^{(k)}(t)$ showed in Eq. (3.212) are fundamentally different from the ones presented in Eq. (3.207) associated with each pure state, $U_\eta^{(k)}(t)$. While the latter is given by the mean values of local observables, the former is represented by the averages of these quantities over the whole system's ensemble. Thus, even though the local effective Hamiltonians $\tilde{H}_\eta^{(k)}(t)$ represent suitable operators for individually characterizing the energetics within possible elements of $\{\hat{\sigma}_\eta^{(0)}(t)\}_\eta$, we did not yet present appropriate local operators for the entire subsystem's internal energy. Along these lines, it is desired to define the operators $\tilde{H}^{(k)}(t)$, such that

$$\langle \tilde{H}^{(k)}(t) \rangle = tr_k\{\tilde{H}^{(k)}(t)\hat{\rho}^{(k)}(t)\} \equiv \sum_{\eta=1}^{d^{(0)}} P_\eta tr_k\{\tilde{H}_\eta^{(k)}(t)\hat{\sigma}_\eta^{(k)}(t)\}, \tag{3.216}$$

or $\sum_{\eta=1}^{d^{(0)}} P_\eta tr_k\{(\tilde{H}^{(k)}(t) - \tilde{H}_\eta^{(k)}(t))\hat{\sigma}_\eta^{(k)}(t)\} = 0$. The simplest way to achieve this is to guarantee

$$\langle \varphi_{\eta j}^{(k)}(t)|\tilde{H}^{(k)}(t)|\varphi_{\eta j}^{(k)}(t)\rangle = \langle \varphi_{\eta j}^{(k)}(t)|\tilde{H}_\eta^{(k)}(t)|\varphi_{\eta j}^{(k)}(t)\rangle, \tag{3.217}$$

for all η and j. As long the equality above is satisfied, the operators $\tilde{H}^{(1,2)}(t)$ are qualified to be the representative observables for quantifying the entire local internal energy, such that

$$U^{(k)}(t) = \langle \tilde{H}^{(k)}(t) \rangle = tr_k\{\tilde{H}^{(k)}(t)\hat{\rho}^{(k)}(t)\}, \tag{3.218}$$

and $U^{(0)} = U^{(1)}(t) + U^{(2)}(t)$.

In short, by identifying the local effective Hamiltonians as the operators that characterize the physical local internal energies, we were able to consistently generalize the expressions presented in Section (3.4) and describe the energetics of general bipartite mixed quantum systems, both at the individual pure state and ensemble levels. As required, these energies are additive and locally accessible. Finally, it is worth highlighting that this procedure is exact and applicable to any setting and regime.

3.8.3.3 Brief remarks

In Section (3.5) it was presented the phase ambiguity inbuilt in the Schmidt decomposition formalism and explained how this gauge freedom influences our calculations and the local effective description. Clearly, it would also play a role in the previous expressions. Nevertheless, considering the discussion shown in Section (3.5.2), we are implicitly assuming the use of the gauges that maintain physical consistency for all the local effective Hamiltonians.

Besides, as mentioned earlier, the identification of appropriate candidates for internal energy is a requirement for defining further thermodynamic quantities. Along these lines, the discussion presented in Section (3.6.3.2) can be entirely imported to the present context of mixed states. Even though we do not introduce work and heat definitions, it provides a consistent framework for beginning a discussion concerning general, exact and symmetrical understanding of work and heat along with any dynamical processes.

3.9 Discussion and summary

In this chapter, it was introduced a novel formalism for describing the energetics within isolated bipartite quantum systems. The formal procedure is based on the well-known Schmidt decomposition and provides a promising route for properly defining effective Hamiltonians and characterizing the subsystem's internal energies in a symmetrical fashion. In contrast with current methodology, such a framework is exact and do not rely on any sort of approximations and additional hypotheses, such as particular coupling regimes, convenient Hamiltonian structures and specific type of dynamics. Surprisingly, despite such generality, this description allows the definition of local properties, i.e., quantities accessible by local observations, that recovers the usual thermodynamic notion of energy additivity. Besides, these expressions also establish a new route for defining further general thermodynamic quantities to the quantum regime, which is also imperative for the design and development of functional quantum devices.

Additionally, from a conceptual perspective, the most common procedures found in the literature of QT are based on semi-classical approaches that are not entirely suitable for a general thermodynamic description of fully autonomous quantum objects. The implicit assumption of a classical agent to externally control and measure the system of interest - and potentially even process this information - restricts QT to this particular semi-classical picture of coherent control where both the quantum nature of the control fields is unimportant to the system's dynamics and the system itself does not change the control's state. Thus, any QT framework that requires an external agent to perform any task, such as driving or measuring the system, is fundamentally limited and phenomenological in spirit. The quantization of this entity is an essential step toward the generalization of QT and the design of autonomous quantum devices. Along these lines, our formalism does not suffer from this shortcoming and, therefore, contributes to further understanding of foundational aspects concerning the development of a fully quantum thermodynamic theory.

The present work focused on the theoretical aspects and viability of the procedure introduced in this chapter. Despite its mathematical consistency and compelling features, a more rigorous analysis on experimental grounds is necessary to support the use of our proposal. In this sense, a detailed examination of the potential physical observations and experiments that one might perform to investigate this framework is out of the scope of this thesis. However, it is of the author's opinion that such deliberation is crucial for building a robust and meaningful physical theory. Thus, let us briefly remark on this topic. Essentially, we associate the local effective Hamiltonian, $\tilde{H}^{(k)}(t) \equiv \sum_{j=1}^{d^{(k)}} \tilde{\epsilon}_j^{(k)}(t)|\tilde{\epsilon}_j^{(k)}(t)\rangle\langle\tilde{\epsilon}_j^{(k)}(t)|$, as the observable for characterizing the physical local internal energy, $U^{(k)}(t)$, of subsystem (k). These operators, by construction, depend on the dynamics of the local Schmidt basis and - a priori - can be experimentally reconstructed once known the time evolution of the local density matrices. Observe that the emergent energetic time dependency clearly implies that the energy spectra $\{\tilde{\epsilon}_j^{(k)}(t)\}_j$ is modified due to the interactions between the subsystems. Notice, however, that this does not happen if the physical internal energy is associated with the bare Hamiltonians $\hat{H}^{(k)}$: clearly, the expectation values might be changing in time, but that would be a consequence of the local state dynamics since the Hamiltonians are constant for autonomous systems, i.e., $\langle\hat{H}^{(k)}\rangle(t) = tr\{\hat{H}^{(k)}\hat{\rho}^{(k)}(t)\}$. In other words, as long as the subsystems are interacting, their eigenenergies are affected by their interaction $\hat{H}_{int}$. Suppose, for instance, a qubit interacting with another object[ap]: on the one hand, the former's bare Hamiltonian could be written as $\hat{H}^{(1)} = \frac{1}{2}\hbar\omega_0\hat{\sigma}_z^{(1)}$, where $\hat{\sigma}_z^{(1)}$ is the usual Pauli matrix, and $\hbar\omega_0$ is the gap between the energy levels; on the other, the local effective Hamiltonian will have the following general structure $\tilde{H}^{(1)}(t) \equiv \frac{1}{2}\hbar\omega_{eff}(t)\tilde{\sigma}_z^{(1)}(t)$, where $\tilde{\sigma}_z^{(1)}(t)$ is the Pauli matrix relative to the time-dependent effective eigenbasis and $\hbar\omega_{eff}(t)$ is the time-dependent effective gap induced by the interaction. Notice that, while in the former, the eigenbasis and energy spectrum are static, in the latter, they are dynamic. Along these lines, as we know, the gap structure dictates the energy frequency absorption and emission, and - in principle

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[ap] In principle, it could be as simple as another two-level system, a single photon, or a complicated body.

- this corresponds to a realistic scenario that could be probed: while the qubit's effective Hamiltonian is changing in time due to the interaction, its absorption frequency $\omega_{eff}(t)$ is also being modulated by subsystem (2), in such a way that its interaction capability with a third party is affected. Similar situations might be constructed considering qutrits and their energy level structures. Essentially, if such a spectrum modulation is observed, it would be in accordance with this work's proposal. Also, it is worth mentioning that this kind of setting and test might be experimentally feasible in optical and solid-state setups and NMR, for instance.

In short, we provided a useful and novel framework for characterizing the energetics within interacting quantum systems. Hopefully, it became clear both the importance of this kind of task and how they are not easy or trivial questions, especially because several subtleties should be considered once more foundational aspects are being raised. Finally, it is - optimistically - expected that these results will also have the potential to motivate the flourishing of new definitions of quantum work and heat, along with the refinement of the understanding of the laws of thermodynamics in the quantum realm.

4 CONCLUSION AND OUTLOOK

Quantum thermodynamics is an exciting and promising research field that will - certainly - play a pivotal role in the design and development of future quantum-based technologies. In addition to the purely practical-driven interests, fundamental theoretical aspects lie at the heart of the intersection of quantum mechanics and thermodynamics. As mentioned earlier, despite many efforts aiming to extend the well-known laws of thermodynamics to the microscopic realm of non-equilibrium and quantum processes, there is still no unifying and general picture for the theory. Along these lines, some fundamental questions remain unanswered. Besides, most current proposals rely on regimes and settings that, although familiar to the macroscopic description, are restrictive to our more ambitious purposes of characterizing the thermodynamics within arbitrary autonomous quantum systems. The present work belongs to this general context.

In this thesis, we focus on the energetic analysis within isolated bipartite quantum systems. More specifically, we propose a novel and general formalism for a dynamic description of the energy exchanges between interacting subsystems. To this aim, instead of using the bare Hamiltonians, we introduce a new effective operator as being the representative element for characterizing the local dynamics and internal energy, i.e., the Schmidt decomposition approach allows the identification of effective Hamiltonians whose expectation values satisfy the desired properties of appropriate definitions of internal energies, namely being local and additive quantities. Such proposal is independent of the Hamiltonian structures (including the interaction term), coupling strengths and other regular constraints, which establishes a promising route for the thermodynamic analysis of general autonomous quantum dynamics[a].

The definition of quantum counterparts of classical thermodynamic variables is one of the core conceptual issues of the field. The identification of quantum thermodynamic entropy, internal energy, work and heat, along with their relationships, is crucial from a foundational point of view and of extreme practical relevance for designing and operating functional quantum devices. Along these lines, our proposal opens up many possibilities for future investigations. A consistent definition of local internal energy corresponds to the first and fundamental step toward the definition of other relevant quantities, especially those directly derived from the energy flow, like work and heat. Consequently, it also provides the means for helping to establish general quantum versions of the first and second laws.

Future research will aim at these topics. However, more importantly, it will also focus on suggesting realistic experimental designs for assessing these quantities and inves-

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[a] The discussions and results introduced in this thesis were presented in (1) after its defense.

tigating our proposal. As discussed earlier, the local effective internal energies are, a priori, experimentally accessible properties. Still, further research is necessary for identifying an appropriate physical setup and the corresponding parameters.

In summary, quantum thermodynamics is a young discipline, and its development is still a work in progress. On the one hand, it implies that it is a fertile field to explore; On the other, it also means there is no solid and cohesive foundation yet. In this thesis, we identify a consistent candidate for quantifying internal energy and provide a simple framework suitable for the energetic analysis of autonomous quantum systems. The proposed formalism does not assume any approximations or restrictive hypotheses, treat the bipartitions on equal footing and is completely general.

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