The Role of Coherences in Quantum Thermodynamics

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The rule is random.

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A mis padres por estar ahí para mi incluso desde la distancia. A Esperanza y su familia por acogerme en su hogar cuando me independicé y por cuidar de mi cuando cuando más lo necesitaba. A Germán Mesías, Sebastián Alvarado y al resto de su grupo de Estadística Avanzada por darme acceso a su estudio detallado del paper de Funo. A Leonel Ardila y J.D. Múñoz por su colaboración en el estudio computacional del teorema de fluctuación clásico. Al profesor Carlos Viviescas y a los miembros del grupo de Caos & Complejidad por las útiles conversaciones e *insights* recibidos a lo largo de los años en los seminarios de grupo y otros espacios. A Felipe Abril por haberme abierto las puertas al mundo de la epidemiología y a Zulma Cucunubá por darme la oportunidad de hacer parte de su gran equipo; me siento afortunado de poder vivir de la investigación en Colombia y es gracias a ustedes.

Resumen

Título en español: El Rol de las Coherencias en la Termodinámica Cuántica

En esta tesis presento una formulación de integrales de camino del esquema de medición Margenau-Hill, el cual permite definir un funcional de trabajo más allá del esquema de dos medidas (TPM), sirviendo como un punto de partida para el estudio del rol de las coherencias en la termodinámica cuántica lo cual ha demostrado ser un asunto apremiante en este campo. El camino hacia este resultado está enmarcado por recientes desarrollos de la física estadística fuera del equilibrio fundamentados en la conexión entre la dinámica estocástica y la termodinámica clásica por medio de la formulación de la estocástica energética y su contraparte cuántica. Resultados claves de esta área suelen expresarse como teoremas de fluctuación, versiones refinadas de la segunda ley de la termodinámica que a su vez permiten realizar predicciones experimentales. Como una contribución original en esta dirección, presento un teorema de fluctuación para el calor que en la transición entre dos estados de equilibrio, a saber, un estado microcanónico inicial que se termaliza tras entrar en contacto con un baño térmico canónico. Volviendo al ámbito cuántico, esta tesis proporciona una descripción detallada del esquema TPM, resaltando sus virtudes y limitaciones, y aclara posibles rutas para superarlas.

Palabras clave: termodinámica cuántica, trabajo, coherencia, teoremas de fluctuación, quasi-probabilidad, integral de camino, observables incompatibles.

Abstract

Título en inglés: The Role of Coherences in Quantum Thermodynamics

In this Thesis I present a path integral formulation of the Margenau-Hill scheme that allows for a definition of a work functional beyond the two point measurement (TPM) scheme, serving as a starting point to assess the role coherences play in quantum thermodynamics, which has proven to be a pressing matter in in this field. The road toward this result is framed by recent developments in statistical physics out of equilibrium, that have been fuelled by the connection achieved between stochastic dynamics and classical thermodynamics under the formulation of stochastic energetics and its quantum counterpart. Key results in this area usually come in the form of fluctuation theorems, i.e. refined versions of the Second Law of Thermodynamics allowing experimental predictions to be made. As a contribution in this direction I present the derivation a novel heat fluctuation theorem describing the transition between two equilibrium states, namely an initial microcanonical state that thermalizes after entering in contact with a canonical thermal bath. Turning to the quantum realm, the Thesis provides a detailed description and analysis of the TPM scheme with its virtues and limitations, and clearly elucidates routes to overcome them.

Keywords: quantum thermodynamics, work, coherence, fluctuation theorems, quasi-probability, path integral, incompatible observables

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1. Introduction

Quantum thermodynamics is an emergent field concerned with the construction of a consistent thermodynamic framework in the quantum regime that allows the extension of key concepts of statistical physics to study open quantum systems. This includes research on quantum thermal machines [1, 2, 3, 4], emergent irreversibility in the quantum regime [5, 6, 7, 8, 9], equilibration and thermalization [10, 11, 12], strongly coupled open systems [13, 14, 15, 16], the role of quantum information in open dynamics [17, 18], among others [17, 19].

As quantum theory has advanced to describe open quantum systems, the formalism of Langevin equations and the subsequent development of stochastic energetics [20] has served as a benchmark to which the quantum counterparts of different quantities must converge in the classical limit to ensure the theory's consistency [19]. Stochastic energetics is the framework that connects stochastic dynamics and classical thermodynamics [20]. This is done by considering the energetic exchanges that occur along single realizations of an stochastic process.

In this context, fluctuation theorems are statistical relations describing the behaviour of the probability distribution function (PDF) of a fluctuating quantity in regards to the relative occurrence of opposite entropy production processes [21, 22]. This relations allow for a detailed description of the statistics of the energetic exchanges occurring out of equilibrium beyond the macroscopic regime of the second law of thermodynamics, thus enabling finer versions of this law capable of describing fluctuations at the mesoscopic scale.

Fluctuation theorems have been shown to describe the transition between different thermal equilibrium states [14, 23]. Moreover, although the Jarzynski equality and other fluctuation theorems have been extended for the microcanonical ensemble [24, 25] and heat fluctuations had also been studied for canonical initial states driven out of equilibrium by the effect of external non-conservative forces [26] as well as for heat exchange between bodies at different initial temperatures [27, 28], a description of heat fluctuations in the transition between the microcanonical and the canonical ensembles is still missing. In section 2.4 I present the derivation of a novel heat fluctuation theorem for a ensemble of independent particles starting at a initial microcanonical state that thermalizes in the stationary limit with a canonical environment at fixed temperature, as well as a simple entropic analysis of the situation.

Given the fact that energy measurements in quantum setups can affect the subsequent measurement of incompatible observables [29, 30], ambiguity in the characterization of quantum stochastic energetic features emerges due to the possibility to implement different schemes to measure or estimate energetic exchanges at the ensemble level or for single realizations of a experiment [31, 32, 33], which pose challenges when trying to generalize concepts from classical stochastic thermodynamics to the quantum regime.

The two-point measurement (TPM) scheme, where work is estimated as the difference between two projective energy measurements performed at the beginning and end of an evolution protocol, has been extensively used to explore work statistics in the quantum regime under external driving [14, 34, 35] . This scheme is thoughtfully explored in chapter 3 along with the quantum foundations necessary to develop the formalism of quantum stochastic thermodynamics. A path integral formulation of the TPM scheme is also presented, where a work functional whose first order approximation corresponds to the classical power definition of work in the semiclassical limit is obtained [13].

Although the TPM scheme is appealing due to the possibility to derive quantum analogues of classical fluctuation relations and results from stochastic thermodynamics [14, 36], a clear limitation subsides in the fact that the first projective measurement inevitably diagonalizes the initial state in the energy basis. This limitation can be subdued by considering alternative schemes relying on weaker notions of measurement (see [37] for a quick summary).

In virtue of a no-go theorem for work, elucidated by Perarnau-Llobet et. al. in [32], different work measurement schemes can be classified depending on whether they reduce to the TPM scheme for incoherent states, i.e. diagonal states in the energy basis, or recovers the energy average change at the ensemble level. It was later shown by Matteo Lostaglio that, in order for a particular scheme to fulfil both conditions simultaneously, work quasiprobabilities (possibly non-positive distributions) or lack of convexity need to be considered [9].

The aforementioned ideas are presented in detail in chapter 4. Furthermore, a particular scheme, namely the Margenau-Hill scheme [38, 39, 40], described by the Margenau-Hill quasiprobability distribution function (QPDF) [41, 42], relying on the estimation of the initial Hamiltonian from a single projective energy measurement at the final time, is described in detail. Moreover, a path integral formulation of this scheme is developed based on the ideas presented in [13, 16], yielding the derivation of a novel representation of the CF in this scheme allowing the distinction between contributions from the populations and coherences of the initial state of the system as well as contributing to the possibility to find a coherent work functional for this particular scheme.

This document serves as an introductory guide to stochastic quantum energetics and contributes to further the understanding of the role that coherences in the initial state play in quantum thermodynamic setups where work definitions consistent with classical stochastic thermodynamics can be considered from the operational perspective of positive-operator valued measures (POVMs) or from equivalent path integral approaches. Furthermore, the fundamental importance of QPDFs to describe quantum fluctuations showcasing strong forms of non-classicality in quantum thermodynamics is highlighted [9].

2. Classical stochastic thermodynamics

In this chapter I explore the classical limit of the quantum thermodynamic framework presented in chapters 3 and 4, serving as a compelling introduction to the conceptual and theoretical tools needed to discuss key concepts such as heat, work and entropy, in both the classical and the quantum domains, addressing their phenomenological motivations as well as their microscopic formal descriptions in the context of stochastic calculus. Here, such quantities are understood as inherently fluctuating ones, which enables the possibility to describe their properties by comparing opposite entropy production processes, yielding the derivation of fluctuation theorems that provide a more detailed statistical description of thermodynamic processes than the one provided by the phenomenological second law of thermodynamics, allowing as well the description of out-of-equilibrium processes. Moreover, I present the derivation of a novel fluctuation theorem for heat for a ensemble of independent harmonic oscillators transitioning from an initial microcanonical state to thermal equilibrium with a canonical environment, first found computationally by L. Ardila and J.D. Múñoz in 2018 by means of molecular dynamics simulations [43].

The chapter is divided as follows. In section 2.1 several thermodynamic concepts are introduced by means of a modern description of phenomenological thermodynamics. In section 2.2 the stochastic formalism describing classical Brownian motion is introduced from a Hamiltonian perspective and a generalized non-Markovian Langevin equation is derived; Wiener processes and the Markov approximation are also discussed. In section 2.3 I explore the stochastic descriptions of important fluctuating quantities and arrive from this perspective to the proper classical functional of work that will be shown later on to correspond to a classical limit for work in the quantum regime. In section 2.4 I show the derivation of some heat fluctuation relations describing transition of a microcanonical ensemble of independent particles to equilibrium with a canonical thermal bath.

2.1. Phenomelogical thermodynamics

Back in the XIX century, in the advent of the industrial revolution, physicists and engineers were primarily interested on the optimization of energetic exchanges undergone by macroscopic systems in contact with one or several environments, such as steam engines [17, 44, 45, 46]. The study of such systems led to the discovery of a set of laws describing

thermal equilibrium as well as transformations between equilibrium states very accurately, regardless of the permanent state of agitation at the microscopic level [45, 47].

Modern formulations of phenomenological thermodynamics describe equilibrium states by means of the equation of state $f(\mathbf{X}) = 0$, which displays the relation between the macroscopic variables $\mathbf{X}$[1] and defines a surface, known as the thermodynamic manifold, where all equilibrium states live [17]. In this context, work and heat are fundamental concepts describing the amount of energy that can be converted into movement and the amount of energy that is exchanged with the environment respectively, leading to the thermodynamic formulation of conservation of energy, namely the First Law of Thermodynamics, which takes the infinitesimal form

$$dU = đQ + đW, \tag{2-1}$$

where $đQ$ and $đW$ are the infinitesimal heat and work respectively and dU represents the internal change of energy. Here the convention that heat and work are positive whenever the internal energy of the system increases is adopted unless otherwise specified. The bar crossing the differentials of heat and work stands for the fact that these quantities are not exact differentials in the sense that they depend on the path taken by the system during its evolution, meaning that there do not exist unique state functions representing these quantities for a given change of the internal energy [45]. In other words, the internal energy only depends on the state of the system $\mathbf{X}$, meanwhile heat and work depend on the specific process done to produce such energy change.

To better illustrate the above point, consider a system described by L generalized coordinates $\mathbf{q} = (q_1, ..., q_L)$ subject to the corresponding generalized forces $\mathbf{F} = (F_1, ...F_L)$. The work exerted on the system over a path C is

$$W := \int_C \mathbf{F} \cdot d\mathbf{q} = \int_C đW, \tag{2-2}$$

where the infinitesimal work is identified as $đW = \mathbf{F} \cdot d\mathbf{q}$. The force $\mathbf{F}$ is said to be conservative only if the work done over a closed path vanishes, i.e. $\oint \mathbf{F} \cdot d\mathbf{q} = 0$; otherwise the force is non-conservative and work depends on the particular path taken by the system during the process.

In 1854, Rudolf Clausius found an equivalent formulation of heat in the form of the inequality [45, 46]

$$\oint \frac{đQ}{T} \leq 0. \tag{2-3}$$

Here, T represents the temperature of the environment and acts as the unique integrating

[1] In the case of an ideal gas $X = (P, V, T)$ and the equation of state is simply $PV - Nk_BT = 0$.

factor allowing the definition of an exact differential for reversible processes [48],

$$dS := \frac{đQ}{T}, \tag{2-4}$$

where S is known as the thermodynamic entropy. The equality in eq. (2-3) holds only when the path taken lies entirely on the surface of the thermodynamic manifold. It is worth noting that, up to this point, temperature is understood as a parameter characterizing equilibrium between systems (allowing for the definition of thermometers in virtue of the zeroth law) and it is not only after the development of statistical mechanics that its relation with average kinetic energy is elucidated.

The Second Law of Thermodynamics, established on the basis of empirical observations by the founders of phenomenological thermodynamics, states that the entropy production of the universe[2] $\Sigma := \Delta S_{tot}$ is always a non-decreasing quantity. Given the extensive nature of thermodynamic entropy, this can be stated as [49]

$$\Sigma = \Delta S_S + \Delta S_B \geq 0, \tag{2-5}$$

where ΔS_S corresponds to the entropy of the system and ΔS_B to that of the bath. Since the state of the environment can safely be assumed to be in an equilibrium state at temperature T, its entropy change can be identified as $-\int đQ/T$, yielding to

$$\Delta S_S \geq \int \frac{đQ}{T}, \tag{2-6}$$

which is yet another form of the Clausius inequality, showing that the second law is an underlying assumption for the derivation of (2-3).

Although the importance of this phenomenological description of thermodynamics, a microscopic description of mechanical systems coupled to thermal environments is still missing. In the following sections an stochastic approach is developed, enabling the study of thermodynamic processes far from equilibrium and elucidating the fluctuating nature of key quantities such as work, heat and entropy that behaves on average as described in this section.

2.2. Brownian motion

At the beginning of the XIX century the Scottish botanist Robert Brown discovered a droplet of water suspended in a piece of quartz. He realized, observing it under the microscope, that

[2] In this context the universe is understood as any system sufficiently isolated from its surroundings, which is assumed in this case for the composite system formed by the thermal environment and the working media.

little particles suspended in the droplet followed irregular trajectories. This resulted familiar thanks to previous observations of a similar phenomena for pollen particles suspended in water. Up to this point his hypothesis was that the movement of the pollen was caused by an inherited vitality from the plant the pollen came from. Under the light of the new observations in the piece of quartz, Brown correctly concluded that his initial hypothesis was incorrect, meaning that this movement was in fact physical in nature, rather than biological [50]. Ever since, this phenomena is commonly known as Brownian motion. By the end of the century, atomic notions of matter were beeing considered and the kinetic theory of gases had already been developed by Clausius, Maxwell and Boltzmann, although by the time atoms were understood more as a convenient mathematical tool rather than real physical objects [51].

It was not until 1905 that Einstein realized that atoms in a fluid would reveal their existence in their effect on suspended larger particles, such as Brown had observed a century ago. Based on the kinetic theory of gases, Einstein found out that the suspended particles suffered measurable changes on their trajectories due to their interaction with the fluid [52, 53]. Later on, in 1910, this was experimentally verified by J. Perrin, who indirectly measured the Avogadro number in agreement to what Boltzmann's kinetic theory had predicted [54]. Thus, the theory of Brownian motion served to demonstrate the discrete nature of matter. Nowadays the theory of Brownian motion can be formulated in as a particular case of stochastic processes described by Langevin equations [55] and still plays fundamental role in our understanding of matter at the microscopic level.

As quantum theory has advanced to describe open quantum systems, the formalism of Langevin equations and the subsequent development of stochastic energetics [20] has served as a benchmark to which the quantum counterparts of different quantities must converge in the classical limit to ensure the theory's consistency [19]. Here I present the main results of the Langevin equations formalism describing classical Brownian motion in a way intended to facilitate comparison with the quantum case and to give a robust stochastic background for the derivation of the heat fluctuation theorem presented in sec. 2.4.

For this, consider a particle of mass M immersed in a thermal environment at inverse temperature $\beta = 1/k_B T$, represented by N microscopic oscillating particles of mass m [3]. Consider as well that the Brownian particle is under the effect of an external force described by a potential $V(\lambda(t), q)$ completely parametrized by the time-dependent parameter $\lambda := \lambda(t)$. As usual, p is the conjugate momentum to the particle coordinate q. Let the position and momentum of the $n-$th bath oscillator be q_n and p_n respectively and ω_n be its frequency,

[3] Where $k_B \approx 1.381 \mathrm{JK}^{-1}$ is the Boltzmann constant and N is of the order of the order of the Avogadro number $N_A = 6.023 \times 10^{23}$.

such that the Hamiltonian of the composite system is given by

$$H = H_{\mathcal{S}} + H_{\mathcal{B}} + H_{\mathcal{SB}}, \tag{2-7}$$

with

$$H_{\mathcal{S}} = \frac{p^2}{2M} + V(\lambda, q), \tag{2-8}$$

$$H_{\mathcal{B}} = \sum_{n=1}^{N} \left(\frac{p_n^2}{2m} + \frac{m\omega_n^2 q_n^2}{2} \right), \tag{2-9}$$

$$H_{\mathcal{SB}} = \sum_{n=1}^{N} \gamma_n \left(\frac{\gamma_n q^2}{2m\omega_n^2} - q_n q \right), \tag{2-10}$$

where $H_{\mathcal{S}}$ is the Hamiltonian of the Brownian particle, $H_{\mathcal{B}}$ is the Hamiltonian of the bath and $H_{\mathcal{SB}}$ is the interaction Hamiltonian.

Formal integration of the associated Hamilton equations along with the assumption that the initial positions and momenta of the microscopic particles conforming the bath follows a canonical distribution,

$$P(\{q_n(0), p_n(0)\}) \sim \exp(-\beta H_B(0)),$$

yields to the following stochastic integro-differential equation for the position of the Brownian particle [20, 56]

$$M\ddot{q} = -\frac{\partial V(\lambda, q)}{\partial q} - \int_0^t \zeta(t-s)\dot{q}(s)ds + \xi_t, \tag{2-11}$$

where

$$\zeta(t) := \sum_{n=1}^{N} \frac{\gamma_n^2}{m\omega_n^2} cos(\omega_n t), \tag{2-12}$$

is a friction like coefficient acting as a memory correlating the state of the Brownian particle at time t with its state at previous times, and ξ_t can be regarded as a random force of zero mean and correlation function

$$\mathrm{E}\left[\xi_t \xi_s\right] = k_B T \zeta(t-s), \tag{2-13}$$

where E[·] stands for the ensemble average over several realizations of the process. For a full derivation of equation (2-11) refer to appendix A. Equation (2-11) is also known as a generalized Langevin equation [57, 58, 59] and it can be extended for multidimensional systems [60, 61, 62]. A common approximation used to avoid the memory effects of the environment is the Markov approximation which, in the context of molecular dynamics, relies on the assumption that the interactions between the particles occur almost instantaneously, meaning

that $\zeta(t)$ decays rapidly in time in comparison with the evolution time-scale of the Brownian particle such that it can be approximated by $\zeta(t) \propto \delta(t)$; the validity of this approximation depends on the relation between the relaxation times of the environment and the Brownian particle, where q and p are expected to vary much slower than the microscopic degrees of freedom of the bath [20].

Although several systems can be described by the Markov approximation [63, 64], whenever the environment has slow-varying degrees of freedom the dynamics of the Brownian particle will be described by a non-Markovian Langevin equation. The simplest example of a non-Markovian process is the Ornstein-Uhlenbeck process, characterized by a exponentially decaying correlation function [65, 66]

$$\zeta(t) = \frac{\gamma}{\tau_c} \exp\left(\frac{-|t|}{\tau_c}\right), \quad \mathrm{E}\left[\xi_t \xi_s\right] = \frac{D}{\tau_c} \exp\left(\frac{-|t-s|}{\tau_c}\right), \tag{2-14}$$

where γ is the damping coefficient, τ_c is the noise correlation time and $D := \gamma k_B T$, yielding to the following familiar Langevin equation [66][4]

$$M\ddot{q} = -\frac{\partial V(\lambda, q)}{\partial q} - \gamma \dot{q} + \xi_t. \tag{2-15}$$

Although equation (2-15) is non-Markovian in general, by means of a suitable change of variables it is possible to recast it as a system of equations with two additional equations for the noise and an additional stochastic variable describing the correlation term, were all stochastic variables are described by Markovian processes [67, 68]; this can be computationally studied by means of molecular dynamic simulations as shown in [69].

A way to determine whether a stochastic process is Markovian is to compare the time increments $|t-s|$ with the Markov-Einstein time scale t_M, that determines the threshold for the time increments above which the Markov approximation is valid. Different methods to estimate this time-scale are presented in chapter 16 of [61]. Under these criteria, for small enough values of τ_c in comparison with the typical time scale of the system τ_s, the Ornstein-Uhlenbeck process tends to be Gaussian, with the correlation function fulfilling the Markov approximation [66, 67]

$$\mathrm{E}\left[\xi_t \xi_s\right] = 2\gamma k_B T \delta(t-s), \tag{2-16}$$

which is justified whenever $t - s >> m/\gamma$ [20]. Moreover, this kind of process can be identified as Wiener processes described by the following stochastic differential equations in

[4] Although this equation may seem like Markovian at first glance, it is non-Markovian due to the dependency of the expectation $\mathrm{E}\left[\xi_t \xi_s\right]$ given by (2-14) depends on both s and t, meaning that when sampling ξ_t at any time, the value of the noise at previous times affects its value.

the Stratonovich prescription[5]

$$dp = -\frac{\partial V(\lambda, q)}{\partial q}dt - \gamma\frac{p}{M}dt + \sqrt{2\gamma k_B T}dB_t, \tag{2-17}$$

$$dq = \frac{p}{M}dt, \tag{2-18}$$

where dB_t represents a white noise with zero mean $E[dB_t] = 0$ satisfying

$$\mathrm{E}\left[dB_t dB_s\right] = 0, \quad \text{for } t \neq s, \tag{2-19}$$

$$dt^2 = 0, \quad dB_t dt = 0, \quad (dB_t)^2 = dt. \tag{2-20}$$

Here the random force ξ_t is related to the normalized stochastic increment $d\beta_t$ through the integral relation $\int_t^{t+dt}\xi_s ds = \sqrt{2\gamma k_B T}dB_t$ [20].

2.3. Stochastic energetics

Stochastic energetics is the framework that connects stochastic dynamics and classical thermodynamics [20]. This is done by considering the energetic exchanges that occur along single realizations of an stochastic process. Consider for instance a system described by Langevin equation in the Markov approximation (see equations (2-17) and (2-18)), written for convenience as

$$\frac{dp}{dt} = -\frac{\partial V(\lambda, q)}{\partial q} - \frac{\gamma}{M}p + \xi_t. \tag{2-21}$$

Note that the total energy of the Brownian particle $\mathcal{S}$ is simply given by

$$U = \frac{p^2}{2M} + V(\lambda, q), \tag{2-22}$$

such that its exact differential in the Stratonovich prescription can be directly computed by means of the chain rule [20]. The exact differential of the kinetic term yields to

$$d\left(\frac{p^2}{2M}\right) = \frac{dp}{dt}\frac{p}{M}dt = \frac{dp}{dt}dq,$$

meanwhile the potential term gives

$$dV(\lambda, q) = \frac{\partial V(\lambda, q)}{\partial q}dq + \frac{\partial V(\lambda, q)}{\partial \lambda}d\lambda.$$

Putting this together, the infinitesimal change of the internal energy of the system $\mathcal{S}$ reads [70, 71]

$$dU = \left(\frac{dp}{dt} + \frac{\partial V(\lambda, q)}{\partial q}\right)dq + \frac{\partial V(\lambda, q)}{\partial \lambda}d\lambda \tag{2-23}$$

$$= \left(-\frac{\gamma}{M}p + \xi_t\right)dq + \frac{\partial V(\lambda, q)}{\partial \lambda}d\lambda, \tag{2-24}$$

[5]Note that both dp and dq represent stochastic quantities even though it is not explicitly noted for convenience. A more adequate notation for these quantities would be dp_t and dq_t.

where equation (2-21) was used. Identifying heat and work as:

$$đQ = \left(-\frac{\gamma}{M}p + \xi_t\right) dq, \tag{2-25}$$

$$đW = \frac{\partial V(\lambda, q)}{\partial \lambda} d\lambda, \tag{2-26}$$

yields to a stochastic statement for the first Law of thermodynamics:

$$dU = đQ + đW. \tag{2-27}$$

Taking a closer look into equations (2-25) and (2-26) it becomes clear that the distinction between work and heat refers to the degrees of freedom that produce the changes of internal energy. Work corresponds to the changes of the parameter λ, which controls the external force acting on the system $\mathcal{S}$ exerted by an external system $\mathcal{W}$ through the interaction potential $V(\lambda, q)$. On the other hand, heat corresponds to the changes in the spatial coordinate of the Brownian particle, which is stochastic in nature. Figure **2-1** shows a schematic representation of the situation.

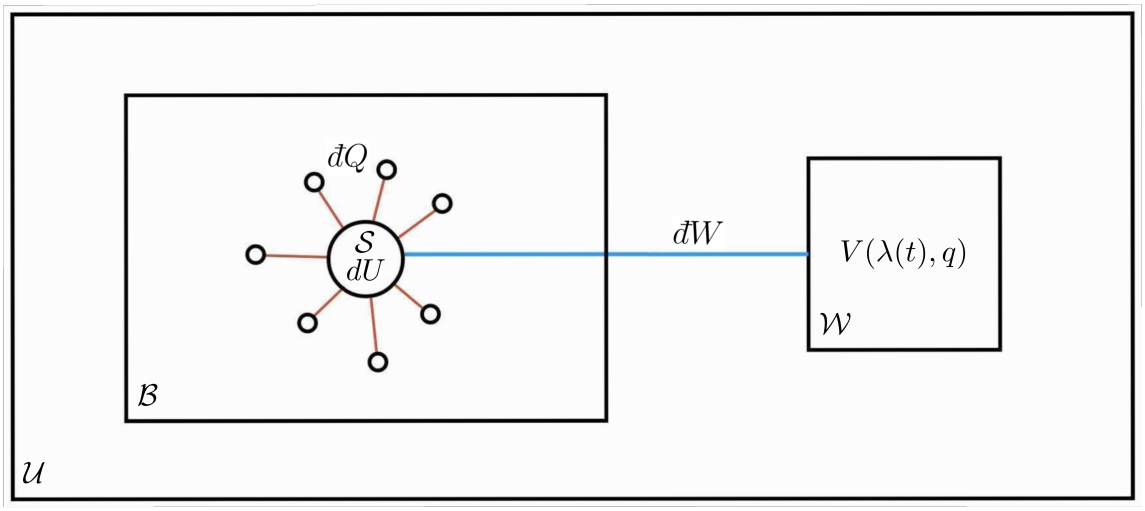


Figure 2-1.: Schematic representation of a Brownian particle $\mathcal{S}$ immersed in a thermal environment $\mathcal{B}$ and coupled to an external work reservoir $\mathcal{W}$ through the potential $V(\lambda, q)$.

Finally, integrating over time the classical functional of work representing the total amount of work performed along a single trajectory gives [13, 20, 70]

$$W_{cl}[q] := \int_0^\tau dt \dot{\lambda} \frac{\partial V(\lambda, q)}{\partial \lambda}. \tag{2-28}$$

This equation corresponds to the classical work functional that different quantum work measurement schemes need to recover for classical states for their thermodynamic descriptions to be consistent with the results of stochastic thermodynamics (see 4.2), such as Crooks' fluctuation theorem [23] and other fluctuation relations [96].

2.4. Heat fluctuations in the transition between the microcanonical and the canonical ensembles

Fluctuation theorems are statistical relations describing the behaviour of the probability distribution function (PDF) of a fluctuating quantity in regards to the relative occurrence of opposite entropy production processes [21, 22]. They allow for a detailed description of the statistics of the energetic exchanges occurring out of equilibrium beyond the macroscopic regime of the phenomenological second law of thermodynamics. Some common known examples are the Jarzyinski equality [72], the Crooks' fluctuation relation [23] and the detailed fluctuation theorem [73], among others [74, 75]. Most fluctuation relations rely on two assumptions: the microreversibility principle, and initial equilibrium with an environment [14].

Here I present the derivation of a Heat fluctuation theorem for a ensemble of independent particles starting in a microcanonical state that thermalizes in the stationary limit with a canonical environment at fixed temperature. Clearly the initial state is far from equilibrium and the microreversibility principle is not explicitely used, although it is implied by the underlying Langevin dynamics.

Consider a microcanonical ensemble formed by N independent particles with energies between E_0 and $E_0 + dE$, with $E_0 >> dE$. At time $t = 0$ the interaction with a Markovian thermal environment at temperature T is activated. In the microscopical sense, this interaction can be modelled by means of harmonic coupling, just as explained in sec. 2.2, such that the stochastic evolution is described by equations (2-17)-(2-20).

After a long time, each particle is expected to thermalize with the environment, reaching a stationary state in such a way that the ensemble describing the final state is canonical. Here the heat fluctuations in this transition between ensembles is investigated and only energy transferences between the heat bath and the particle are considered.

Under the aforementioned conditions, the heat exchanged along a single stochastic trajectory q_t is given by

$$\Delta Q[q_t] = \Delta U = E_f - E_i, \tag{2-29}$$

where E_i and E_f are the initial and final energy of a particle following the stochastic trajectory. Since work is not being exerted on the system, heat is simply the total energy transferred by the heat bath to the particle. The PDF of heat can thus be built up as

follows

$$\begin{aligned} P(Q) :&= \int dz_i dz_f P(z_i, z_f)\delta(Q - (E_f - E_i)), \\ &= \int dz_i dz_f P(z_i) P(z_f|z_i)\delta(Q - (E_f - E_i)), \end{aligned} \tag{2-30}$$

where $z = (q, p)$ corresponds to the phase space position of the Brownian particle and $P(z_i, z_f)$ gives the joint distribution for the initial and final states. As done in the second line of equation (2-30), it is convenient to factorize the joint probability distribution as the product between the initial condition of the ensemble $P(z_i) = \Omega^{-1}\delta(H_{\mathcal{S}}(z_i) - E_0)$ and the conditional probability $P(z_f|z_i)$ by means of the Bayes theorem. Besides, once the state has reach thermal equilibrium with the environment, achieving a final energy E_f, the conditional term in the stationary limit in equation (2-30) corresponds to the canonical distribution $P(z_f|z_i) = Z_{\mathcal{B}}^{-1} \exp(-\beta E_f)$, which is independent of the initial condition of the system $\mathcal{S}$. Replacing this in eq. (2-30) yields to

$$\begin{aligned} P(Q) &= \frac{1}{Z_{\mathcal{B}}} \int dz_f \exp(-\beta E_f)\, \delta(Q - (E_f - E_0)) \\ &= \beta \exp(-\beta(Q + E_0)), \end{aligned} \tag{2-31}$$

where $\Omega = 1$, because the initial position and momentum can be measured with certainty on each run, and $Z_{\mathcal{B}} = \beta^{-1}$ is obtained normalizing the canonical distribution. Note that the minimal heat transfer possible occurs whenever the system reaches a stationary state with null final energy, meaning that $Q_{min} = -E_0$ and it remains negative in the interval $0 \leq E_f < E_0$, meanwhile whenever $E_f \geq E_0$ the system absorbs energy from the environment and the heat transfer is non-negative.

Besides, proportion of events where the system absorbs energy ($Q > 0$) against the events where the system gives up energy to the environment ($Q < 0$) can be computed by direct integration of eq. (2-31):

$$\begin{aligned} \frac{P(Q > 0)}{P(Q < 0)} &= \frac{\int_0^\infty P(Q)dQ}{\int_{-E_0}^0 P(Q)dQ} \\ &= \frac{1 - \exp(-\beta E_0)}{\exp(-\beta E_0)} \\ &= \exp(\beta E_0) - 1. \end{aligned} \tag{2-32}$$

This proportion depends on the relation between the energy of the initial microcanonical ensemble and the energy scale of the heat bath $k_B T$. Whenever $E_0 > k_B T \ln(2)$ for most of the repetitions of the experiment the system will absorb energy from the environment and vice-versa. In a similar fashion the probabilities for opposing heat transfer events to occur

can be compared

$$\frac{P(Q)}{P(-Q)} = \exp(-2\beta Q). \tag{2-33}$$

This fluctuation relation is valid in the range $-E_0 < Q < 2E_0$ and shows that there is a privileged direction for heat transfer which is exponentially more likely than the other.

Moreover, the average entropy production can be computed noting that the initial entropy is zero, given that ideally there is not uncertainty about the initial state, and computing the final entropy from the canonical free energy $F = \beta^{-1}\ln(\beta)$:

$$\begin{aligned}\Delta S &= k_B \ln(\Omega) - \left(-\frac{\partial F}{\partial T}\right) \\ &= k_B T\left(\ln(k_B T) + 1\right).\end{aligned} \tag{2-34}$$

These results give insight on the probabilistic behaviour of a system undergoing thermalization; furthermore, they glimpse the possibility to study systems transitioning between different statistical ensembles from the perspective of fluctuation theorems and characterize the entropy production of the thermalization process.

3. Introduction to quantum thermodynamics

This chapter serves as an introduction to the study of microscopic energetics in the quantum regime and its interplay with quantum information theory in the form of quantum resource theories (QRTs), taking as a starting point the well known quantum measurement theory [76, 77] and building up the necessary concepts to assess the role of initial coherence in thermodynamic processes.

An important task in quantum thermodynamics consists on the characterization of work and heat in the quantum domain. A common approach to this problem, known as the two-point measurement (TPM) scheme, consists on performing two projective measurements of energy at the beginning and at the end of a given evolution protocol [34, 49]. The TPM protocol is typically used as a benchmark to describe the work statistics for incoherent initial states, given that it allows for the derivation of fluctuation theorems equivalent to those of classical stochastic thermodynamics[14].

This is chapter is divided as follows: In sec. 3.1 an introduction to quantum measurement theory in terms of positive operator-valued measures (POVMs) is presented. In sec. 3.2 I review aspects of the resource theory of coherence, including the definition of incoherent sates and transformations, as well as coherence quantifiers in terms of Krauss operators. In sec. 3.3 the TPM scheme along with its corresponding work statistics is presented; moreover an introduction to the path integral approach to the TPM scheme by Funo et. al. [13, 16] is studied in detail, arriving to the work functional correspondence with eq. (2-28) in the classical limit.

3.1. Quantum measurement theory

The contemporary canonical description of quantum measurements is built upon the concepts of operations and effects [49, 77, 78]. In 1961 E. C. G. Sudarshan et. al. [79] described quantum dynamical maps as a general form of stochastic transformations for the density matrix for open systems. The notion of operations in the context of the algebraic formulation of quantum mechanics [80] was introduced by Rudolf Haag and Daniel Kastler in 1963 [81], where operations are understood as the action of a physical apparatus over a system

during a finite time, resulting in the transformation of a state into another. In 1968, K.-E. Hellwig and K. Kraus [82] furthered this ideas, resulting in the formulation of operations in terms of a set of Hermitian operators that eventually came to be known as Kraus operators. In 1970 E.B. Davies and J.T. Lewis [83] reached similar conclusions abandoning von Neumann's repeatability hypothesis introducing the concept of instruments and relying on a Hilbert space structure for the state space. Nowadays quantum operations and effects are usually used as key components of the measurement postulate of quantum theory as means to describe the effect of general measurements performed over a quantum system [77].

3.1.1. Quantum operations

Here I start by introducing the measurement postulate in terms of measurement operators relying on the unitary dynamics of closed quantum systems as is canonically presented in [77].

Let $\{M_n\}_{n=0}^{N-1}$ be a set of measurement operators such that $\sum_n M_n^\dagger M_n = \mathbb{1}$ and $|\psi\rangle \in \mathcal{H}$ be a pure state. Then the probability to obtain outcome n when a measurement is performed is given by[1]

$$\mathcal{P}(n) = |M_n |\psi\rangle|^2 = \langle\psi| M_n^\dagger M_n |\psi\rangle . \tag{3-1}$$

Given result n as the result of a measurement, the state of the system collapses to

$$|\psi\rangle \to |\psi_n'\rangle = \frac{M_n |\psi\rangle}{\sqrt{\mathcal{P}(n)}}. \tag{3-2}$$

The measurement is said to be projective if $M_n^\dagger M_n = M_n$ [84]. Equation (3-2) describes the post-measurement state when the system is described by a pure state, meaning that there is not classical uncertainty about the state of the system previous to the measurement. Whenever this is not the case, the state of the system is described by a mixed state, i.e. a classical ensemble of pure states $\{P(i), |\psi_i\rangle\}$, such that the state of the system can be represented by

$$\rho = \sum_i P(i) |\psi_i\rangle \langle\psi_i| , \tag{3-3}$$

where $P(i)$ are the ensemble probabilities of the mixture fulfilling $\sum_i P(i) = 1$. Note that given a measurement result n each member of the classical ensemble collapses to

$$\rho_i = |\psi_i\rangle \langle\psi_i| \to \rho_i' = \frac{M_n \rho_i M_n^\dagger}{P(n|i)} \tag{3-4}$$

[1] Here I differentiated probabilities of quantum origin by $\mathcal{P}$ from from inherently classical probabilities, denoted by P.

with conditional probability $P(n|i) = \mathrm{Tr}\left[M_n^\dagger M_n \rho_i\right]$, which represents the probability to obtain a measurement result n given that the state ρ_i is chosen from the ensemble. According to the rule of total probability [85], the probability to obtain outcome n for mixed states is

$$\begin{aligned}\mathcal{P}(n) &= \sum_i P(i)\mathcal{P}(n|i) \\ &= \mathrm{Tr}\left[M_n^\dagger M_n \sum_i P(i)\rho_i\right] \\ &= \mathrm{Tr}\left[M_n^\dagger M_n \rho\right]. \end{aligned} \tag{3-5}$$

From equations (3-2) and (3-5) we can write the density matrix representations of the a posteriori state as

$$\rho_n' = \frac{M_n \rho M_n^\dagger}{\mathrm{Tr}\left[M_n^\dagger \rho M_n\right]}. \tag{3-6}$$

As is to be expected, the state of the system after the measurement is still mixed. Furthermore, the new classical ensemble can be found explicitly by means of equation (3-4)

$$\begin{aligned}\rho_n' &= \frac{1}{\mathcal{P}(n)} \sum_i P(i) M_n \rho_i M_n^\dagger \\ &= \sum_i \frac{P(i)\mathcal{P}(n|i)}{\mathcal{P}(n)} \left(\frac{M_n |\psi_i\rangle}{\sqrt{\mathcal{P}(n|i)}}\right)\left(\frac{M_n |\psi_i\rangle}{\sqrt{\mathcal{P}(n|i)}}\right)^\dagger, \end{aligned} \tag{3-7}$$

meaning that the new state of the system is given by the ensemble

$$\left\{\frac{P(i)\mathcal{P}(n|i)}{\mathcal{P}(n)}, \frac{M_n |\psi\rangle}{\sqrt{\mathcal{P}(n|i)}}\right\} \tag{3-8}$$

It is clear from equations (3-6)-(3-8) that the new mixed state of the system is conditioned to the result of the measurement. This is because from the very beginning the choice to record the result of the measurement was done implicitly. This kind of measurements are known as selective or stochastic operations [86]. On the other hand, if the process associated to a measurement operator occurred but the result of the measurement was not recorded, either by choice or practical limitations, then the representation of the state would be

$$\rho' = \sum_n \mathcal{P}(n)\rho_n' = \sum_n M_n \rho M_n^\dagger, \tag{3-9}$$

which is known as a non-selective operation and corresponds to a completely positive and trace-preserving map (CPTP)[86]. Note that the maps $\mathcal{C}_n = M_n \rho M_n^\dagger$ take operators into operators; these are known as super-operators [78]. The set of operators $\{M_n\}$ is known as a positive operator-valued measure (POVM) and it fixes the statistics of measurements for both selective and non-selective operations.

3.2. The resource theory of coherence

3.2.1. Introduction to quantum resource theories

A resource theory is specified by setting constrains over the allowed transformations, also called free transformations, that a system can undergo. These constrains may be fundamental, like the speed of light or the first and second laws of thermodynamics, or practical, like limited access to the fuel needed to move a machine or even limited access to financial resources in an economical context [87]. In particular, quantum resource theories (QRTs) deal with free operations defined by imposed restrictions over the set of all possible quantum operations that may act on a system.

To illustrate this, let $\mathcal{H}$ be the Hilbert space associated to a possibly multipartite system described by the global Hamiltonian H and let $\Gamma = \mathcal{H} \otimes \mathcal{H}'$ be the set of all possible density states of the system, where $\mathcal{H}'$ is the dual space of $\mathcal{H}$, and let $\mathcal{A}$ be the set of allowed (free) operations. All states $\sigma \in \mathcal{F} \subset \Gamma$ that can be prepared by means of free operations alone are called free states, meanwhile the remaining states in $\mathcal{R} = \Gamma \setminus \mathcal{F}$ are called resources [88].

Let $\rho, \sigma \in \Gamma$ be density matrices and define the relation $\succ_{\mathcal{A}}$ as [87]

$$\rho \succ_{\mathcal{A}} \sigma \quad \text{iff} \quad \exists \mathcal{E} \in \mathcal{A} : \quad \mathcal{E}(\rho) = \sigma. \tag{3-10}$$

The relation $\succ_{\mathcal{A}}$ induces a partial ordering in Γ in the sense that it can be used to distinguished what states can be converted into others by means of free operations. This way, the free states are defined as those states that can be prepared by means of a free operation regardless of the initial state. Moreover, the existence of this relation enables the construction of monotones, i.e. real valued functions that preserves the partial order induced by $\succ_{\mathcal{A}}$. For a particular monotone $M : \Gamma \to \mathbb{R}$ the following implication holds [88]

$$\text{if} \quad \rho \succ_{\mathcal{A}} \sigma \to M(\rho) \geq M(\sigma). \tag{3-11}$$

This allows to quantify aspects of the underlying resource at play by means of the monotone M.

The QRT of entanglement was the first to be developed [89, 90], for which the set of free operations are restricted to be the class of local operations and classical operations (LOCC) [87, 91]. Ever since, other QRTs have been developed to tackle several features of quantum systems such as coherence [86, 92, 93] and thermalization [6, 88], among many others [87].

3.2.2. Coherence as superposition

According to the superposition principle of quantum mechanics, the state of a quantum system can in general be represented as a proper superposition between other possible states.

Take for instance a two level system, i.e. a qubit, whose first two energy levels are represented by $|0\rangle$ and $|1\rangle$. Then, any other pure state can be written as

$$|\psi\rangle = \alpha_0 |0\rangle + \alpha_1 |1\rangle , \tag{3-12}$$

where $\alpha_i \in \mathbb{C}$ and $|\alpha_0|^2 + |\alpha_1|^2 = 1$. Writing the complex amplitudes in polar form $\alpha_i = e^{i\theta_i}|\alpha_i|$ yields

$$\begin{aligned} |\psi\rangle &= e^{i\theta_0} \left(|\alpha_0| \, |0\rangle + e^{i(\theta_1 - \theta_0)} |\alpha_1| \, |1\rangle \right) \\ &= |\alpha_0| \, |0\rangle + e^{i\Delta_{10}} |\alpha_1| \, |1\rangle , \end{aligned} \tag{3-13}$$

where I defined $\Delta_{10} := \theta_1 - \theta_0$ and set $\theta_0 = 0$ without lose of generality[2]. Thus, the state of the two level system is completely parametrized by the real numbers $|\alpha_0|, |\alpha_1|$ and $\Delta_{01} \in [0, 2\pi]$. Eq. (3-13) is what is known as a coherent superposition in the computational basis $\{|0\rangle, |1\rangle\}$ [77] and we refer as coherence to the underlying quantum feature characterizing such interference phenomena.

The density matrix representation of ψ can be written as

$$\rho_\psi = |\psi\rangle \langle\psi| = \begin{pmatrix} |\alpha_0|^2 & |\alpha_0||\alpha_1| e^{i\Delta_{12}} \\ |\alpha_1||\alpha_0| e^{-i\Delta_{12}} & |\alpha_1|^2 \end{pmatrix} , \tag{3-14}$$

where the phase differences $\Delta_{ij} := \theta_i - \theta_j$ were defined. This can easily be extended to K-level systems. by considering an arbitrary pure state in the computational basis $\{|k\rangle\}_{k=0}^{K}$:

$$|\Psi\rangle = \sum_{k=0}^{K-1} e^{i\theta_k} |\alpha_k| \, |k\rangle = e^{i\theta_{k'}} \sum_{k=0}^{K-1} e^{i\Delta_{kk'}} |\alpha_k| \, |k\rangle , \tag{3-15}$$

where $k' \in [0, K-1]$. Representing the state as a density matrix gives

$$\begin{aligned} \rho_\Psi = |\Psi\rangle \langle\Psi| &= \sum_{kl} |\alpha_k||\alpha_l| e^{i\Delta_{kk'}} e^{-i\Delta_{lk'}} \, |k\rangle \langle l| \\ &= \sum_{kl} A_{kl} e^{i\Delta_{kl}} \, |k\rangle \langle l| , \end{aligned} \tag{3-16}$$

where $A_{kl} = |\alpha_k||\alpha_l|$ is defined and I used the relation $\Delta_{ij} = -\Delta_{ji}$. Note that the density matrix ρ_Ψ is independent of the global phase $e^{i\theta_{k'}}$ factorized initially. Explicitly distinguishing between the diagonal and the off-diagonal contributions to ρ_Ψ,

$$\rho_\Psi = |\Psi\rangle \langle\Psi| = \sum_k |\alpha_k|^2 \, |k\rangle \langle k| + \sum_{k \neq l} A_{kl} e^{i\Delta_{kl}} \, |k\rangle \langle l| , \tag{3-17}$$

it becomes clear that the off-diagonal elements of ρ_Ψ are essential for the description of coherence since they encapsulate the relative phase between the basis elements and the interplay between their amplitudes, meanwhile the diagonals, commonly refer to as the populations, coincide with the probabilities to obtain the respective outcomes under projective measurements.

[2] Note that the states $|\psi\rangle = |\alpha_0| \, |0\rangle + e^{i\Delta_{12}} |\alpha_1| \, |1\rangle$ and $|\psi'\rangle = e^{i\phi} \left(|\alpha_0| \, |0\rangle + e^{i\Delta_{12}} |\alpha_1| \, |1\rangle \right)$ share the same density matrix representation, i.e. $|\psi\rangle \langle\psi| = |\psi'\rangle \langle\psi'|$

3.2.3. Incoherent states and operations

So far in this section I have only been concerned with pure states. However, whenever there is uncertainty about the state of the system, this is represented by a mixed state, i.e. a classical ensemble of pure states $\{P(i), |\psi_i\rangle\}$, where $P(i)$ represents the probability for the state to be prepared at $|\psi_i\rangle$. Mixed states can be represented as convex sums in the density matrix representation:

$$\rho_{\{P(i),|\psi_i\rangle\}} = \sum_i P(i) \, |\psi_i\rangle \langle\psi_i| \, . \tag{3-18}$$

Note that if each $|\psi_i\rangle \langle\psi_i| = |i\rangle \langle i|$ were to be projectors in a computational basis, the state would be diagonal in the sub-space of Γ spanned by the set $\{|\psi_i\rangle\}$, meaning that it would lack coherence in this particular (possibly incomplete) basis in the sense discussed before. This fact is exploited to define incoherent states, i.e. the free states of the QRT of coherence, also known as incoherent states.

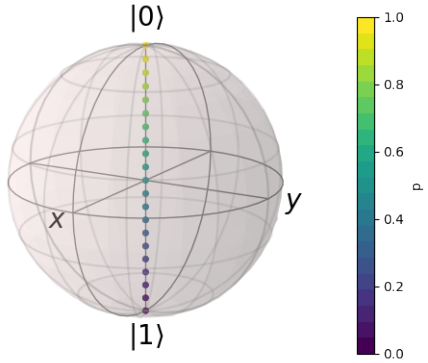


Figure 3-1.: Bloch sphere representation of incoherent states for a two level system. Here, the colorbar represents the value of the probability $p \in [0, 1]$ to sample the state at $|0\rangle$, such that the state can be represented as $\rho = p \, |0\rangle \langle 0| + (1 - p) \, |1\rangle \langle 1|$

For this, consider a quantum system with an N-dimensional Hilbert space $\mathcal{H}$ and let $\{|n\rangle\}_{n=0}^{N-1}$ be our preferred basis for $\mathcal{H}$. Then, the set of all incoherent states with respect to this basis is defined as [86]

$$\mathcal{I}_{\{|n\rangle\}} = \left\{ \delta \in \Gamma = \mathcal{H} \otimes \mathcal{H}' : \quad \delta = \sum_{n=0}^{N-1} \delta_n \, |n\rangle \langle n| \right\} \tag{3-19}$$

where $\mathcal{H}'$ represents the dual of $\mathcal{H}$ as before and $\sum_n \delta_n = 1$. For the particular case of a two level system, the incoherent states can be identified as those in the vertical axis in the Bloch sphere representation (see fig. **3-1**).

Given the definition of free states for the QRT of coherence, the free operations can be identified as those that take incoherent states into incoherent states. Consider an operation $\{M_j\}$ in the sense of sec. 3.1.1; this operation is said to be incoherent if [86]

$$M_j \delta M_j^\dagger \in \mathcal{I} \quad \forall \delta \in \mathcal{I}. \tag{3-20}$$

Two examples of these are the dephasing channel, specified by:

$$K_0(\epsilon) = \sqrt{1-\epsilon}\mathbb{1}, \quad K_1(\epsilon) = \frac{\sqrt{\epsilon}}{2}(\sigma_z + \mathbb{1}), \quad K_2(\epsilon) = \frac{\sqrt{\epsilon}}{2}(\sigma_z - \mathbb{1}); \tag{3-21}$$

and the damping channel:

$$K_0(\eta) = \frac{1}{2}(\sigma_z + \mathbb{1}) + \frac{\sqrt{1-\eta}}{2}(\mathbb{1} - \sigma_z), \quad K_1(\eta) = \frac{1}{2}(\sigma_x + i\sigma_y), \tag{3-22}$$

where $\epsilon, \eta \in [0, 1]$ and σ_i are the Pauli matrices. For a detailed prove that these channels correspond to incoherent operations refer to [94].

3.2.4. Coherence quantifiers

The idea behind the definition of coherence quantifiers is based on the existence of the monotones described in sec. 3.2.1. Let $C : \Gamma \to \mathbb{R}$ be a monotone of the QRT of coherence. Some properties that C should have in order to be consider a proper coherence measure have been proposed in the literature [86, 92, 93]. The most common are:

i) Non-negative for all density operators and null only for incoherent states:

$$C(\rho) \geq 0 \quad \forall \rho \in \Gamma \quad \text{and} \quad C(\sigma) = 0 \quad \text{iff} \quad \sigma \in \mathcal{I}. \tag{3-23}$$

ii) Monotonicity under non-selective incoherent CPTP maps (see. sec 3.1.1):
Let $\{M_j\}$ be a CPTP operation such that $M_j \mathcal{I} M_j^\dagger \subseteq \mathcal{I}$. Then

$$C(\rho) \geq C(\sum_j M_j \rho M_j^\dagger), \quad \forall \rho \in \Gamma. \tag{3-24}$$

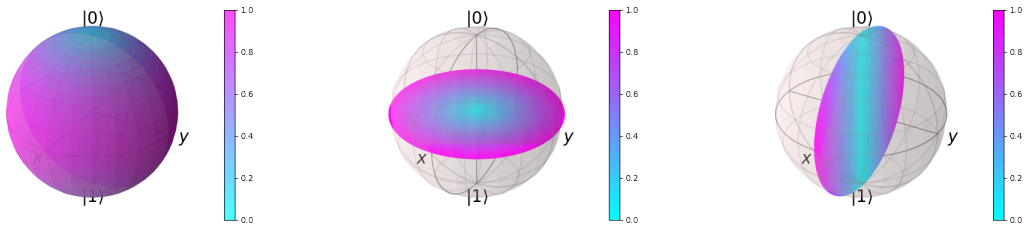
iii) Non-increasing under mixing (convexity):
Let ρ be a mixed state specified by the ensemble $\{P(i), \rho_i\}$. Then

$$\sum_i P(i) C(\rho_i) \geq C(\sum_i P(i)\rho_i) \tag{3-25}$$

An important coherence measure that sufies all practical purposes of this work is the one induced by the l_1-norm, denoted as C_{l_1}, which is simply defined as follows [86]

$$C_{l_1}(\rho) = \sum_{i \neq j} |\rho_{ij}|, \tag{3-26}$$

which simply corresponds to summing over the norm of all off-diagonal elements of the density matrix ρ. The value of C_{l_1} over different sections of the Bloch sphere for a two level system can be seen in fig **3-2**.



(a) (b) (c)

Figure 3-2.: Value of the coherence quantifier C_{l_1} for a two level system over (a) the surface, (b) the $x-y$ plane and, (c) the vertical plane perpendicular to the y axis of the Bloch sphere.

3.3. The two-point measurement scheme

Consider an isolated driven quantum system $\mathcal{S}$ subject to the effect of an external driving described by the potential $V(\lambda, X)$, where X represents a position-like operator and $\lambda := \lambda(t)$ specifies the time dependency of the external driving. The Hamiltonian of this system is

$$H_{\mathcal{S}}(\lambda) = \frac{1}{2M}P^2 + V(\lambda, X), \tag{3-27}$$

where M is the mass of the system and P is the conjugated momentum of X[3]. This system can be coupled to a thermal environment $\mathcal{B}$ by means of an interaction Hamiltonian $H_{\mathcal{SB}}$. The total Hamiltonian now reads

$$H = H_{\mathcal{S}}(\lambda) + H_{\mathcal{B}} + H_{\mathcal{SB}}, \tag{3-28}$$

where $H_{\mathcal{B}}$ represents the Hamiltonian of the bath.

It is to be expected, in contrast to the classical case, that the driving protocol $\lambda(t)$ injects or extracts work into or out of the system according to energy balance. Moreover, it is expected for work in the quantum regime to be a path dependent process given that it is not a state function in the thermodynamical sense, such that it should not be represented by a Hermitian

[3]Note that here I am denoting operators by capital letters and eigenvalues by lowercase unless otherwise stated, meaning that $P|p\rangle = p|p\rangle$ and $X|x\rangle = x|x\rangle$ represent the eigenvalue equations for momentum and position respectively.

operator whose eigenvalues can be determined by a single projective energy measurement [34]. This rules out the possibility to define a meaningful operator of work by means of the total change of the Hamiltonian along the process, as was suggested in [31, 95], if one wants to describe work for single realizations of an experiment. Furthermore, the work operator approach fails to fulfill the Jarzynski equality unless the Hamiltonian commutes with itself at different times ($[H(\lambda(t)), H(\lambda(\tau))] = 0$) [14, 31]. This is further discussed in sec. 4.1.

A first attempt to overcome this limitations is the TPM scheme [34, 35, 36], according to which work is defined as the difference between two projective energy measurements over the system at different times. Here it is worth noting a subtle point regarding to what is understood as the internal energy of the system. The definition of work can vary depending on whether the internal energy of the system is measured as the eigenstates of the unperturbed Hamiltonian of the system alone (exclusive work) or taking into account the effect of the external driving as part of the internal energy of the system (inclusive work) [96]. For the remaining of this document the inclusive definition of work is adopted.

The eigenvalue equation for the Hamiltonian of the system for an outcome k at time t reads $H_{\mathcal{S}} |k, \lambda(t)\rangle = E_k^t |k, \lambda(t)\rangle$. Suppose that an initial projective measurement of energy at time $t = 0$ gives the outcome E_n^0. After a time $t = \tau$ a second projective measurement of energy is performed with a result E_m^τ. The inclusive work over a single realization of this experiment can thus be identified as

$$w_{nm}^{TPM} := E_m^\tau - E_n^0. \tag{3-29}$$

The PDF of this fluctuating quantity is given by the joint probability to perform the corresponding consecutive projective measurements of the energy. This PDF can be built up by summing the probabilities to obtain all possible combinations of n and m giving as a result that a certain amount of work W was performed over the system [13, 14]

$$\begin{aligned} \mathcal{P}^{TPM}(w) &:= \sum_{nm} \mathcal{P}(n,m)\delta(w - w_{nm}^{TPM}) \\ &= \sum_{nm} \mathcal{P}(m|n)\mathcal{P}(n)\delta(w - w_{nm}^{TPM}), \end{aligned} \tag{3-30}$$

where $P(m|n)$ corresponds to the conditional probability of measuring E_m^τ given that the initial measurement gave E_n^0 as a result, i.e. the transition probability between the two energy states

$$\mathcal{P}(m|n) = \left| \langle E_m^\tau | U_{\mathcal{S}} | E_n^0 \rangle \right|^2, \tag{3-31}$$

and the probability to measure E_n^0 is given by $\mathcal{P}(n) = \mathrm{Tr}\left[\Pi_{E_n^0} \rho_{\mathcal{S}}(0)\right]$, where $\Pi_{E_n^0} = |n, \lambda(0)\rangle \langle n, \lambda(0)|$, $\rho_{\mathcal{S}}$ is the initial state of the system and $U_{\mathcal{S}}$ is the time ordered unitary evolution operator [13]

$$U_{\mathcal{S}} = \mathcal{T} \exp\left(-\frac{i}{\hbar} \int_0^\tau dt H_{\mathcal{S}}(\lambda(t)) \right), \tag{3-32}$$

where $\mathcal{T}$ stands for the time-ordering operator. According to equation (3-2), the post measurement state just after the first projective measurement is

$$\frac{\Pi_{E_n^0}\rho_{\mathcal{S}}(0)\Pi_{E_n^0}}{\mathcal{P}(n)}, \tag{3-33}$$

which is diagonal in the energy basis, meaning that any subsequent process the system may undergo after this measurement will not account for the initial coherence of the system.

Another interesting aspect of the TPM scheme lies in the possibility to write equation (3-30) in terms of POVMs [97]

$$\mathcal{P}^{TPM}(w) = \mathrm{Tr}\left[\rho_{\mathcal{S}} M(w)\right], \tag{3-34}$$

where $M(w) := \sum_{nm} \mathcal{P}(m|n)\delta(w - w_{nm}^{TPM})\Pi_{E_n^0}$. This ensures the existence of an instrument that produces an output w with probability $\mathcal{P}^{TPM}(w)$ that can be constructed by virtue of the unitary dilation theorem unitarily coupling the system to a proper ancilla and performing projective measurements on it [49][4].

3.3.1. Path integral approach to the TPM scheme

In 2018 Funo & Quan formulated a path integral approach to the TPM scheme for both isolated and open quantum systems. In their approach, the work [13] and heat [16] characteristic functions (CFs) are expressed as path integrals. This allows the identification of the functional of quantum work for this particular scheme, which resembles a power integral. Moreover, the right classical limit of the work functional (eq. (2-28)) can be shown to coincide with the first term of the semiclassical expansion of the quantum work functional for the TPM scheme and further terms of the expansion correspond to quantum corrections that can be calculated to any order in the conjugated time (defined below) for single realizations [13]. Here I present this formalism in detail aiming to develop the tools needed to find the path integral representation for the alternative scheme presented in 4, where the projective measurements of the TPM scheme are replaced by a single measurement at the end of the protocol and the initial energy is estimated from it, which turns out to be equivalent to weakly measure the initial energy.

[4] Here an instrument is understood as a set of completely positive, trace non-increasing and convex linear super-operators acting on the Hilbert space of the system. The unitary dilation theorem states that if an operation can be written as a sum representation of the members of an instrument (see eq. (3-9) for instance), then there exist a extension of the Hilbert space of the system $\mathcal{H}_{SA} := \mathcal{H}_S \otimes \mathcal{H}_A$, where the operation can be written in terms of only unitary transformations in the joint Hilbert space $\mathcal{H}_{SA}$ and projections in the ancilla space $\mathcal{H}_A$. See sec. 1.5 of [49] for a more detailed discussion.

The CF of work in an arbitrary scheme can be calculated as the Fourier transform of the corresponding PDF

$$\chi_w(\nu) := \int dw \mathcal{P}(w) \exp\left(\frac{i}{\hbar}\nu w\right). \tag{3-35}$$

Not only the PDF of work is fully characterized by means of the inverse Fourier transform of the CF; all moments of work can also be computed by derivation of equation (3-35) [13, 98]

$$\mathrm{E}[w^k] = i^{-k}\left[\frac{d^k}{d\nu^k}\chi_w(\nu)\right]. \tag{3-36}$$

The PDF is determined by the particular measurement scheme being consider. For the TPM scheme, the CF is computed by replacing (3-30) into (3-35) (setting $\hbar = 1$) (3-35)

$$\begin{aligned}
\chi_w^{TPM}(\nu) &= \sum_{nm} \mathcal{P}(m|n)\mathcal{P}(n) \exp\left(i\nu w_{nm}^{TPM}\right) \\
&= \sum_{nm} \langle E_m^\tau| U_\mathcal{S} |E_n^0\rangle \langle E_n^0| U_\mathcal{S}^\dagger |E_m^\tau\rangle \langle E_n^0| \rho_\mathcal{S}(0) |E_n^0\rangle \exp\left(i\nu w_{nm}^{TPM}\right) \\
&= \sum_{nm} \langle E_m^\tau| U_\mathcal{S} e^{-i\nu E_n^0} |E_n^0\rangle \langle E_n^0| \rho_\mathcal{S}(0) |E_n^0\rangle \langle E_n^0| U_\mathcal{S}^\dagger e^{i\nu E_m^\tau} |E_m^\tau\rangle \\
&= \mathrm{Tr}\left[U_\mathcal{S} e^{-i\nu H_\mathcal{S}(\lambda(0))} \left(\sum_n \Pi_{E_n^0} \rho_\mathcal{S}(0) \Pi_{E_n^0}\right) U_\mathcal{S}^\dagger e^{i\nu H_\mathcal{S}(\lambda(\tau))}\right] \\
&= \mathrm{Tr}\left[e^{-i\nu H_\mathcal{S}(\lambda(0))} \mathcal{D}[\rho_\mathcal{S}(0)] e^{i\nu \bar{H}_\mathcal{S}(\lambda(\tau))}\right]
\end{aligned} \tag{3-37}$$

where $\bar{H}_\mathcal{S} = U_\mathcal{S}^\dagger H_\mathcal{S} U_\mathcal{S}$ is the Heisenberg representation of the Hamiltonian and $\mathcal{D}[A] := \sum_k \Pi_k A \Pi_k$ represents the dephasing operator, that reflects the effect of the protocol on the initial coherences of the system and ν is set to have units of time, thus called the conjugate time.

The path integral representation of equation (3-37) reads (see Appendix B for a detailed derivation)

$$\begin{aligned}
\chi_w^{TPM}(\nu) := \int dx_i dy_i dx_f dy_f \delta(x_f - y_f) \int Dx \int Dy^* \\
\rho_0^{diag}(x_i, y_i) \exp\left(\frac{i}{\hbar}\left(S_2^\nu[x] - S_2^\nu[y]\right)\right) \exp\left(i\frac{\nu}{\hbar} W_\nu^{TPM}[x]\right)
\end{aligned} \tag{3-38}$$

where the path integral is defined as

$$\int Dx = \lim_{K,L\to\infty} \int dx_\nu \int dx_0 \cdots dx_K \int dx_0' \cdots dx_L' \left(\frac{M}{2\pi i\hbar dt}\right)^{\frac{K+L+2}{2}}, \tag{3-39}$$

and $\rho_0^{diag}(x_i, y_i) := \langle x_i| \mathcal{D}[\rho_\mathcal{S}(0)] |y_i\rangle$. The action $S_2^\nu[x]$ is defined as

$$S_2^\nu[x] := S[x] + \int_\tau^{\tau+\nu} dt' \mathcal{L}[\lambda(\tau), x(t')] \tag{3-40}$$

with $S[x] := \int_0^\tau dt' \mathcal{L}[\lambda(t'), x(t')]$ being the action along a single path $x(t) := x$, and the Langragian of the system is simply $\mathcal{L}[\lambda(t), x] = \frac{M}{2}\left(\frac{dx}{dt}\right)^2 - V[\lambda(t), x]$. More importantly, the quantum work functional for the TPM scheme reads:

$$W_\nu^{TPM}[x] := \int_0^\tau dt \frac{\dot{\lambda}(t)}{\nu} \int_0^\nu dt' \frac{\partial}{\partial \lambda(t)} V[\lambda(t), x(t'+t)]. \tag{3-41}$$

corresponding to equation (B-26) of Appendix B. This definition is such that the work functional resembles the form of the classical functional of work given by equation (2-28) and it depends only of the potential $V[\lambda(t), x(t)]$ and the driving protocol $\lambda(t)$. Moreover, by expanding the inner integral in equation (3-41) with respect to the conjugate time ν, it can be shown that in the classical limit the $W_\nu^{TPM}[x]$ reduces to the classical functional of work. Calculating said expansion explicitly:

$$\begin{aligned}
\int_0^\nu dt' \frac{\partial}{\partial \lambda(t)} V[\lambda(t), x(t'+t)] =& \sum_{n=0}^{\infty} \frac{\nu^n}{n!} \left(\frac{\partial^n}{\partial \nu^n} \int_0^\nu dt' \frac{\partial}{\partial \lambda(t)} V[\lambda(t), x(t+t')] \right)\Bigg|_{\nu=0} \\
=& 0 + \nu \left(\left(\frac{\partial}{\partial \nu} \nu \right) \frac{\partial}{\partial \lambda(t)} V[\lambda(t), x(t+\nu)] \right)\Bigg|_{\nu=0} + \\
& \sum_{n=2}^{\infty} \frac{\nu^n}{n!} \frac{\partial}{\partial \lambda(t)} \left(\frac{\partial^n}{\partial \nu^n} V[\lambda(t), x(t+\nu)] \right)\Bigg|_{\nu=0} \\
=& \nu \frac{\partial}{\partial \lambda(t)} V[\lambda(t), x(t)] + \sum_{n=2}^{\infty} \frac{\nu^n}{n!} \frac{\partial}{\partial \lambda(t)} \left(\frac{\partial^n}{\partial \nu^n} V[\lambda(t), x(t+\nu)] \right)\Bigg|_{\nu=0}
\end{aligned}$$

where the derivative of the integral was computed by means of the Leibniz rule (see eq. (B-23) in Appendix B)

$$\begin{aligned}
W_\nu^{TPM}[x(t)] =& \int_0^\tau dt \frac{\dot{\lambda}(t)}{\nu} \left[\nu \frac{\partial}{\partial \lambda(t)} V[\lambda(t), x(t)] + \frac{\nu^2}{2} \frac{\partial}{\partial \nu} \left(\frac{\partial}{\partial \lambda(t)} V[\lambda(t), x(t+\nu)] \right)\Bigg|_{\nu=0} + \right. \\
& \left. \frac{\nu^3}{3!} \frac{\partial^2}{\partial \nu^2} \left(\frac{\partial}{\partial \lambda(t)} V[\lambda(t), x(t+\nu)] \right)\Bigg|_{\nu=0} + \cdots \right] \\
=& W_{cl}[x(t)] + \sum_{n=1}^{\infty} W_n^{TPM}[x(t); \nu].
\end{aligned} \tag{3-42}$$

Here, $W_{cl}[x(t)]$ corresponds to the classical work functional derived in sec. 2.3 (see equation (2-28)) and the quantum corrections are given by

$$W_n^{TPM}[x(t); \nu] := \frac{\nu^n}{(n+1)!} \int_0^\tau dt \dot{\lambda}(t) \left(\frac{\partial^{n+1}}{\partial \lambda(t) \partial \nu^n} V[\lambda(t), x(t+\nu)] \right)\Bigg|_{\nu=0}. \tag{3-43}$$

By means of equation (3-43) the first quantum correction to the TPM work functional can

be computed:

$$\begin{aligned} W_1^{TPM}[x(t),\nu] =& \frac{\nu}{2}\int_0^\tau dt \frac{\partial}{\partial\lambda(t)}\left(\frac{\partial x(t+\nu)}{\partial\nu}\frac{\partial}{\partial x(t+\nu)}V[\lambda(t),x(t+\nu)]\right)\Big|_{\nu=0} \\ =& \frac{\nu}{2}\int_0^\tau dt\dot{\lambda}(t)\dot{x}(t)\frac{\partial^2}{\partial\lambda(t)\partial x(t)}V[\lambda(t),x(t)], \end{aligned} \tag{3-44}$$

which can be calculated explicitly when both the external potential $V[\lambda(t),x(t)]$ and the path $x(t)$ are specified.

4. Beyond the TPM scheme and the role of initial coherence

Although the TPM scheme has proven to be of useful to understand the statistical properties of work and heat in the quantum regime, due to the projective nature of the initial measurement it is not a proper definition of work to address the role that coherences in the initial state of the system may have on its microscopic energetics. Circumventing this fundamental limitation is of utmost importance to address the role that this quantum correlation plays in quantum thermodynamic processes [37].

Since energy measurements can perturb the subsequent evolution of a quantum system, it is to be expected for ambiguity to emerge when considering alternative ways to measure energy instead of projective measurements. Different protocols to measure quantum work can be classified thanks to a no-go theorem by Perarnau-Llobet et. al. [32] according to which a consistent protocol based on PDFs either i) gives the difference of average internal energy for closed quantum systems or ii) reduces to the TPM scheme for incoherent initial states. Protocols fulfilling condition ii) are referred to as fluctuation theorem protocols (FTPs) [9] given that the TPM scheme has been shown to be successful in describing fluctuation theorems for diagonal states in the energy basis and recovering their corresponding classical limit [14, 37].

However, there are alternative definitions of work able to fulfil conditions i) and ii) simultaneously at the expense of positivity in the distribution of work[9], meaning that for these approaches the statistics of work is described by quasi-probability distribution functions (QPDFs), i.e. probability distributions that can take negative values. Moreover, it has been shown that allowing for negativities in the work statistics enables stronger forms of non-classicality due to restrictions arising from the incompatibility of the Hamiltonian at different times when only work distributions are considered [9]. Some examples of QPDFs in quantum mechanics are the Wigner function [99, 100], the Keldish QPDF [101], the Kirkwood-Dirac QPDF [102], and the Margenau-Hill distribution [38, 41, 42], which corresponds to the real part of the Kirkwood-Dirac QPDF[102].

This chapter is divided as follows: In sec. 4.1 I compare the TPM scheme with an earlier attempt to define work in the quantum regime, namely the work observable approach [31,

95, 103], under the light of a quantum fluctuation theorem for the CF of work in the TPM scheme and briefly review some important alternative definitions of work that had been developed in recent years. In sec. 4.2 the no-go theorem by Perarnau-Llobet et. al. [32] and a particular reformulation by Matteo Lostaglio [9] are discussed in order to understand how QPDFs describing the work statistics inevitably emerge in this context when considering FTPs for which the average change of energy coincides with work for closed systems. Finally, in sections 4.3.1 and 4.3.2 the work statistics in the Margenau-Hill scheme, a particular FTP, is explored as well as its corresponding path integral formulation.

4.1. The TPM scheme vs the work observable approach

A reason why the TPM scheme is an appealing approach to define work in the quantum regime is due to its statistical resemblance with classical stochastic thermodynamics, represented by the emergence of equivalent fluctuation theorems. To illustrate this point, consider a quantum system described by the time dependent Hamiltonian $H(\lambda(t))$ that is in contact with a thermal bath at inverse temperature β, meaning that the initial state of the system is

$$\rho(0) = \frac{1}{Z(\lambda(0))} e^{-\beta H(\lambda(0))}, \tag{4-1}$$

where $Z(\lambda(t)) = \mathrm{Tr}\left[e^{-\beta H(\lambda(t))}\right]$ is the partition function. At time $t = 0$, the coupling between the system and the environment is shut down, such that the system evolves unitarily until $t = \tau$, when a second projective measurement of energy is performed and the interaction with the bath is activated, yielding to a final equilibrium state characterized by $Z(\lambda(t))$.

From equation (3-37), is easy to show that the characteristic function in this case is

$$\chi_W^{TPM}(\nu;\lambda) = \frac{1}{Z(\lambda(0))} \mathrm{Tr}\left[U(0,\tau;\lambda) e^{-i(\nu+\beta)H(\lambda(0))} U^\dagger(0,\tau;\lambda) e^{i\nu H(\lambda(\tau))}\right], \tag{4-2}$$

where I adopt the notation $U(0,\tau) := U(0,\tau;\lambda)$ to specify that the unitary evolution operator is evaluated along the forward protocol $\lambda(t)$. The objective now is to characterize the irreversible nature of this kind of process. For this, it is necessary to properly describe the time inverted evolution for quantum systems. This can be done by means of the anti-unitary time reversal operator (TRO) Θ and the quantum microreversibility principle (MRP), given by [104, 14]

$$U(0,\tau;\lambda)^\dagger = U(\tau,0;\lambda) = \Theta^\dagger U(0,\tau;\tilde{\lambda})\Theta, \tag{4-3}$$

corresponding to equation (C-12) of Appendix C evaluated at time $t = 0$. The effect of the TRO is to properly invert the direction of momentum-like degrees of freedom of the system and the quantum MRP describes how to correctly invert the time dependency of a system in order to describe backward trajectories, i.e. trajectories starting from the final state of the system following the backward evolution protocol $\tilde{\lambda}(t) = \lambda(\tau - t)$. For a more detailed

descriptions of these concepts refer to Appendix C.

Replacing (4-3) in the CF (4-2) and remembering that $\Theta\Theta^\dagger = 1$

$$\chi_w^{TPM}(\nu;\lambda) = \frac{1}{Z(\lambda(0))}\mathrm{Tr}\left[\Theta^\dagger U(0,\tau;\tilde{\lambda})\Theta e^{i\nu H(\lambda(\tau))}\Theta^\dagger U^\dagger(0,\tau;\tilde{\lambda})\Theta e^{-i\nu H(\lambda(0))}e^{-\beta H(\lambda(0))}\Theta^\dagger\Theta\right]. \tag{4-4}$$

Since $\Theta i = -i\Theta$, then $\Theta A\Theta^\dagger = A^\dagger$ for an arbitrary operator A, equation (4-4) can be written as

$$\begin{aligned} Z(\lambda(0))\chi_w^{TPM}(\nu;\lambda) &= \mathrm{Tr}\left[\Theta^\dagger U(0,\tau;\tilde{\lambda})e^{-i\nu H(\lambda(\tau))}U^\dagger(0,\tau;\tilde{\lambda})e^{i\nu H(\lambda(0))}e^{-\beta H(\lambda(0))}\Theta\right] \\ &= \mathrm{Tr}\left[e^{-i(\nu+i\beta)H(\lambda(0))}U(0,\tau;\tilde{\lambda})e^{i\nu H(\lambda(\tau))}U^\dagger(0,\tau;\tilde{\lambda})\right] \\ &= \mathrm{Tr}\left[e^{-i(\nu+i\beta)H(\lambda(0))}U(0,\tau;\tilde{\lambda})e^{-i(-\nu+i\beta)H(\lambda(\tau))}e^{-\beta H(\lambda(\tau))}U^\dagger(0,\tau;\tilde{\lambda})\right] \end{aligned} \tag{4-5}$$

Finally, comparing equations (4-2) and (4-5), the well known Tasaki-Crooks relation for the characteristic function of work in the TPM scheme is obtained [14]

$$Z(\lambda(0))\chi_w^{TPM}(\nu;\lambda) = Z(\lambda(\tau))\chi_w^{TPM}(-\nu+i\beta;\tilde{\lambda}). \tag{4-6}$$

By means of the Fourier transform it is easy to prove the Tasaki-Crooks quantum fluctuation theorem:

$$\frac{\mathcal{P}^{TPM}(w;\lambda)}{\mathcal{P}^{TPM}(-w;\tilde{\lambda})} = e^{\beta(w-\Delta F)}, \tag{4-7}$$

where the free energy is defined as $\Delta F = \beta^{-1}\ln\left(Z(\lambda(\tau))/Z(\lambda(0))\right)$.

Although its relevance for the development of the field, the TPM protocol presents some fundamental limitations due to the projective nature of the measurements involved. In particular, the first projective measurement diagonalize the state in the energy basis, eliminating all coherences from the start, such that their effect on the subsequent energetic evolution of the system is suppressed from the very beginning of the protocol [105, 106].

Earlier attempts to describe work in the quantum regime relied on the notion of an operator of work [31, 95, 103], also known as work observable, denoted here by $\hat{W}$. This operator can be straightforwardly identified considering the average energy change between times $t = 0$ and $t = \tau$, denoted by $\Delta U = \tilde{W}$, for a closed system described by a time dependent Hamiltonian $H(t)$

$$\langle w\rangle := \mathrm{Tr}\left[\rho(\tau)H(\tau) - \rho(0)H(0)\right] = \mathrm{Tr}\left[\rho(0)\tilde{W}\right], \tag{4-8}$$

where $\langle w\rangle$ is the average work and the *work observable* $\tilde{W} := U^\dagger H(\tau)U - H(0)$ is defined. An appealing consideration of this approach is the fact that a power like expression for $\tilde{W}$

can be obtained under the effect of a particular evolution protocol $\lambda(t)$ [31, 95]

$$\tilde{W} = \int_0^\tau dt' \frac{\partial \lambda}{\partial t'} \frac{\partial H}{\partial t'}. \tag{4-9}$$

Moreover, the work operator approach is consistent with phenomenological thermodynamics in the sense that for closed systems it is to be expected that any energy change should come in the form of work [32, 45].

Here, a discrepancy between these two approaches can already be elucidated. Meanwhile the TPM scheme yields to a characteristic function specified by a time ordered correlation function (see eq. (3-37))

$$\chi_w^{TPM}(\nu) = \mathrm{Tr}\left[e^{-i\nu H(\lambda(0))}\mathcal{D}[\rho(0)]e^{i\nu \bar{H}(\lambda(\tau))}\right], \tag{4-10}$$

which can be measured for single realizations of the experiment[34], the work observable approach defines the average work as the expectation value of an operator, which can be experimentally accessed by measuring the ensemble average of energy at the beginning and end of the evolution protocol[31], meaning that this definition of work does not depend on the particular path followed by the system along the evolution.

This discrepancy between the TPM scheme and demanding that average work coincides with the average change of energy for closed systems clearly shows the difficulty to design universal work measurements [37]. In fact, as a consequence of the no-go theorem presented in [32], FTPs can overcome this limitation only if the distribution describing the work statistics is allowed to present negative values or lacks convexity [9, 37]; this will be explored in detail in the following section.

4.2. No-go theorem for quantum work

Due to operational advantages and to the fact that fluctuation theorems are recovered by the TPM scheme, this approach has been extensively used as a first attempt to describe stochastic energetics in the quantum regime [14]. However, it comes in short when attempting to describe fluctuations of work for coherent quantum systems, which has motivated the exploration of a broad spectrum of work definitions that allow for initial superposition states to be considered without the need to project the state to an energy eigenstate at the beginning of the evolution protocol[39, 105, 107, 108, 109], thus allowing to assess the role of initial coherence on the statistics of work.

The discrepancy between the definition of work provided by TPM scheme and the one based on a work observable presented in 4.1 has been extensively discussed along the development

of quantum thermodynamics [31, 32, 34]. In 2017 Perarnau-Llobet et. al. proved a no-go theorem addressing this issue [32]. This result states that any given definition of work that can be characterized by a PDF $\mathcal{P}(w)$ cannot simultaneously fulfill the following two conditions:

i) The average of work for closed quantum systems corresponds to the average change of energy for all initial states $\rho(0)$, i.e.

$$\sum_w w\mathcal{P}(w) = \mathrm{Tr}\left[\rho(\tau)H(\tau) - \rho(0)H(0)\right], \tag{4-11}$$

meaning that a work operator can be defined (see eq. (4-9)).

ii) For incoherent states in the energy basis $\rho \in \mathcal{I}$, the statistics of work along individual trajectories should reduce to that of the TPM scheme, meaning that the results from classical stochastic thermodynamics are recovered (see for instance the Tasaki Crooks fluctuation theorem derived in sec. 4.1).

Each one of these conditions are meant to impose over quantum work to be reasonably in agreement with the classical limit. Condition i) requires that the energy measurements performed to compute the average work do not perturb the system enough to affect the subsequent statistics, thus agreeing with the phenomenological behavior of work for closed systems; meanwhile condition ii) requires that the results from stochastic thermodynamics for work fluctuations are recovered for classical (incoherent) states. The fact that any definition of work whose statistics is described by a positive distribution cannot simultaneously fulfill both conditions seems to be a fundamental restriction impose by quantum mechanics [32]. This is to say that either we renounce to a microscopic description of work consistent with classical stochastic thermodynamics or we must accept that energy measurements perturb the system so much that the first law of phenomenological thermodynamics is violated for closed systems.

It is worth noting that the no-go theorem as presented in [32] strongly relies on the assumption that the distribution describing work statistics is always positive. However, some approaches to define work were already found to be described by QPDFs [39, 40, 105], although an interpretation for negativities present in the quasi-distributions lacked interpretation. This possibility can be accounted for by considering an additional third condition for the no-go theorem [9, 37]:

iii) Let $\mathcal{P}^P(w|\rho_0^i) \geq 0$ be the probability to measure work under a given protocol P[1] conditioned to the initial state $\rho_i(0)$. Then $\mathcal{P}^P$ should be convex under mixtures of

[1]Here the protocol P can correspond to a label for any specific measurement protocol, e.g. $P =$ TPM would correspond to the TPM scheme, $P =$ MH to the Margenau-Hill scheme, etc. A extensive list of possible protocols can be found at the end of this section.

differing initial preparations, e.g. for an arbitrary mixture of $\rho_1(0)$ and $\rho_2(0)$, given by $\rho(0) = p\rho_1(0) + (1-p)\rho_2(0)$, with $p \in [0,1]$, the following should hold

$$\mathcal{P}(w|\rho(0)) = p\mathcal{P}(w|\rho_1(0)) + (1-p)\mathcal{P}(w|\rho_2(0)). \tag{4-12}$$

This condition is violated whenever the distribution $\mathcal{P}$ lacks convexity or corresponds to a QPDF.

Taking into consideration condition iii) the no-go theorem can be stated as [37]

Theorem 1: There exist no protocol P to measure quantum work that simultaneously satisfies conditions i), ii) and iii) for all $\rho(0)$ and $H(\lambda(t))$.

Under the light of *theorem 1*, it has been shown that any FTP satisfying condition iii) can be explained by classical non-contextual model[2][9], which represents a restriction to study strong forms of non-classicality in the quantum regime [29, 110]. This motivates the use and exploration of FTPs described by QPDFs for which a clear statistical interpretation of its negative values is still lacking, although they had been shown to be witnesses of contextuality [9] and to be related with the violation of Leggett-Garg iequalities [101, 111].

For the sake of completeness, some alternative definitions of work developed in recent years are listed below:

- *Margenau-Hill scheme:* This scheme is based on the idea of replacing the first projective measurement of the TPM scheme by an estimation of the initial Hamiltonian from a single projective measurement at the end of the evolution protocol [39]. In this case the statistics of work is described by the Margenau-Hill QPDF [38, 40], which can be described in terms of pseudo-projectors (PP) [30, 112]. The work statistics of this

[2]It is worth clarifying what is meant by non-contextuality at least at a superficial level. Similarly as for the case of locality, contextuality is a concept closely related to the notion of ontological models - also refer to as *hidden-variable models* - i.e. a model relying on the assumption that physical systems specified by a set of (possibly unknown) parameters, known as the ontic state, exist and that these are subject to experimentation regardless of our knowledge about them [29]. Now, considering an operational interpretation of quantum mechanics where the instructions to be implemented in a laboratory can be decomposed into preparation procedures, transformation procedures and measurement procedures[29], non-contextuality refers to situations where all similar instructions, i.e. instructions that are distributed the same for every ontic state, are indistinguishable operationally[37]. This means that, in non-contextual models, the underlying (ontic) state of the system is not affected by the way we decide to prepare it or measure a certain property of it (transformations are usually incorporated as part of preparation and measurement procedures). A more detailed discussion about contextuality and its relation to strong forms of non-classicality is out of the scope of this document, although I encourage the reader to check references [29, 110, 37, 9] for an introduction to the subject. In particular, the first Appendix of [9] discusses the relation between contextuality and FTPs to measure work.

scheme is presented in sec. 4.3.1 and its path integral formulation is explored in sec. 4.3.

- *Full counting statistics (FCS) scheme:* The FCS scheme considers the behavior of a time dependent operator whose eigenstates are used to described the transition probabilities to go from the initial to the final state [105]. By constraining a given functional associated to the paths, the evolution of the whole system is described by a effective Hamiltonian similar to the linear coupling used to describe weak measurements [39, 84]. In [113], the work statistics in the FCS scheme is investigated and the effects of initial coherences are addressed. This scheme is described by a QPDF [114].

- *Continuous monitoring along quantum trajectories:* For quantum systems described by the Lindblad master equation (i.e. Markovian dynamics and rotating wave approximation), an stochastic Schrödinger equation can be used to unravel the dynamics for individual trajectories [49, 78]. Identifying work as the unitary contribution to the stochastic master equation and heat as its non-unitary contribution, a infinitesimal first law of quantum stochastic thermodynamics can be formulated [107, 115] for which feedback loops can be experimentally implemented [107, 116]. Here, the total energy change along single trajectories can be compared to the TPM result in the unitary case [116] and negative probabilities can appear for both work and heat contributions in the corresponding transition probabilities for initial superposition states[107].

- *Bayesian networks approach*[108]*:* In this case, heat exchange in a bipartite correlated system is explored by means of dynamic Bayesian networks built upon the conditional probability of the local energy eigenstates of each party given the state of the global system. Although this scheme does not rely on the use of QPDF for the statistic of work, it does lack additivity over mixtures of different preparations of the initial state [33].

- *End point measurement (EPM) protocol:* Similarly to the Margenau-Hill scheme, the EPM protocol defines work based only on a single projective measurement of energy at the final time [109]. However, in this case the initial energy is not estimated, but rather the initial state is prepared in a known (possibly mixed) state, meaning that the PDF of the initial energy can be known; in fact, for this scheme to be implemented, the initial energy should be measured for some repetitions of the experiment to make sure that the initial energy is distributed as expected. A nice feature of this scheme is that it resembles the way quantum computers work and experimental verification for its predictions have been obtained using the IBMQ platform [109]. It is worth noting that this approach fails to recover the TPM statistics for incoherent states but reproduces the average energy change for closed systems, in accordance with the no-go theorem for work.

4.3. The Margenau-Hill scheme

In this section I explore the Margenau-Hill scheme, an alternative to the TPM scheme consisting of replacing the first projective measurement by an estimation of the initial Hamiltonian based on a single projective measurement at the end of the evolution protocol. Since the Hamiltonian at different times may not commute, this cannot be done with certainty. However, following the ideas in [39, 117], the best possible estimate of the initial Hamiltonian that can be obtained from this projective measurement can be computed minimizing a suitable mean square difference. Moreover, the value of the estimate corresponds to a weak value of the initial energy [39]. This is known as the Margenau-Hill scheme, given that the work statistics in this case is given by the Margenau-Hill QPDF. This scheme has extensively been studied in recent years [33, 38, 40].

4.3.1. Work statistics under the Margenau-Hill scheme

Consider the same situation as at the beginning of section 3.3. In order to prescind from the first projective energy measurement of the TPM scheme, consider only that the second measurement takes place. Rather than projectively measure the energy at time $t = 0$, we want to infer the statistics of the initial energy based on the results obtained from measuring the energy at time $t = \tau$. Let $\bar{H}_{\mathcal{S}} = \sum_m E_m^\tau U_{\mathcal{S}}(\tau)^\dagger \Pi_{E_m^\tau} U_{\mathcal{S}}(\tau)$ be the Heisenberg representation of the final Hamiltonian and $\rho_{\mathcal{S}}(0)$ be an initial arbitrary state of the system. Then, the best representation of the initial Hamiltonian $H_I = \sum_n E_n^0 \Pi_{E_n^0}$ in terms of the projectors $\bar{\Pi}_{E_m^\tau}$ can be constructed minimizing the following mean square difference [39, 117]

$$\mathrm{Tr}\left[\rho_{\mathcal{S}}(0)\left(f(\bar{H}_F) - H_I)^2\right)\right], \tag{4-13}$$

where $f(\bar{H}_F) = \sum_m f_m \bar{\Pi}_{E_m^\tau}$, with $\bar{\Pi}_{E_m^t}$ being the Heisenberg representation of the energy m-th eigen-projector at time t. It has been shown elsewhere [117] that the minimum possible statistical deviation is achieved when f_m correspond to generalized weak values [118]

$$\begin{aligned} f_m :=& \frac{\mathrm{Re}\left\{\mathrm{Tr}\left[\bar{\Pi}_{E_m^\tau}\rho_{\mathcal{S}}(0)H_I\right]\right\}}{\mathrm{Tr}\left[\bar{\Pi}_{E_m^\tau}\rho_{\mathcal{S}}(0)\right]} \\ =& \sum_n E_n^0 \mathcal{P}^{MH}(n|m), \end{aligned} \tag{4-14}$$

where

$$\mathcal{P}^{MH}(n|m) := \frac{\mathrm{Re}\left\{\mathrm{Tr}\left[\bar{\Pi}_{E_m^\tau}\Pi_{E_n^0}\rho_{\mathcal{S}}(0)\right]\right\}}{\mathrm{Tr}\left[\bar{\Pi}_{E_m^\tau}\rho_{\mathcal{S}}(0)\right]}. \tag{4-15}$$

Note that the denominator in eq. (4-15) corresponds to the probability to measure E_m^τ, meaning that the numerator can be identified as a joint QPDF in virtue of the Bayes rule of probability

$$\mathcal{P}^{MH}(n,m) := \mathrm{Re}\left\{\mathrm{Tr}\left[\bar{\Pi}_{E_m^\tau}\Pi_{E_n^0}\rho_{\mathcal{S}}(0)\right]\right\}, \tag{4-16}$$

which recovers the right marginal distributions:

$$\sum_n \mathcal{P}^{MH}(n,m) = \mathrm{Tr}\left[\rho_{\mathcal{S}}(0)\bar{\Pi}_{E_m^\tau}\right], \quad \sum_m \mathcal{P}^{MH}(n,m) = \mathrm{Tr}\left[\rho_S(0)\Pi_{E_n^0}\right]. \tag{4-17}$$

Furthermore, since $\mathrm{Re}\{A\} = \frac{1}{2}(A + A^\dagger)$, is easy to show that equation (4-16) yields

$$\mathcal{P}^{MH}(n,m) = \frac{1}{2}\mathrm{Tr}\left[\rho_{\mathcal{S}}(0)\left(\bar{\Pi}_{E_m^\tau}\Pi_{E_n^0} + \Pi_{E_n^0}\bar{\Pi}_{E_m^\tau}\right)\right]. \tag{4-18}$$

$\mathcal{P}^{MH}(n,m)$ is known as the Margenau-Hill distribution [42], who realized how negative joint probabilities emerge when considering the correlations between the results of consecutive measurements of non-commuting observables back in 1961. However, some years before this, in 1957, A.O. Barut had come to similar results when trying to construct an operator representing the right joint density distribution of incompatible observables [41, 119].

In close analogy to (3-30), the QPDF of work can be built [40]

$$\mathcal{P}^{MH}(w) = \sum_{nm} \mathcal{P}^{MH}(n,m)\delta(w - (E_n^0 - E_m^\tau)). \tag{4-19}$$

To illustrate that $\mathcal{P}^{MH}(n,m)$ actually corresponds to a QPDF, lets find a set of lower an upper bounds for equation (4-18).

Denoting for convenience the initial and final Hamiltonians as $A := H_{\mathcal{S}}(\lambda(0))$ and $B := U_{\mathcal{S}}^\dagger H_{\mathcal{S}}(\lambda(\tau))U_{\mathcal{S}} = \bar{H}_{\mathcal{S}}(\lambda(\tau))$, such that their spectral decompositions are

$$A = \sum_n a_n \Pi_{a_n}, \quad B = \sum_m b_m \bar{\Pi}_{b_m}; \tag{4-20}$$

and defining

$$\Pi_{a_n b_m} := \frac{1}{2}\left(\Pi_{a_n}\bar{\Pi}_{b_m} + \bar{\Pi}_{b_m}\Pi_{a_n}\right), \tag{4-21}$$

the QPDF of work in the Margenau-Hill scheme, given by eq. (4-18), can be recast as

$$\mathcal{P}^{MH}(n,m) := \mathrm{Tr}\left[\Pi_{a_n b_m}\rho\right]. \tag{4-22}$$

The object $\Pi_{a_n b_m}$ is often refer to as a pseudo-projector (PP) [112] or as the Hermitian product between Π_{a_n} and $\bar{\Pi}_{b_m}$ [120]. Two important properties of these objects are worth noting: (a) for two incompatible observables, PPs possess at least one negative eigenvalue (see eq. (39) of [39] for an example); and (b) the PPs corresponding to all possible joint outcomes form an over-complete set as a consequence of the completeness of the set of projectors of each observable [121].

Note that, since $\Pi_{a_n}^2 = \Pi_{a_n}$ and $\bar{\Pi}_{b_m}^2 = \bar{\Pi}_{b_m}$, their eigenvalues are either 0 or 1. Thus, the following inequalities hold

$$0 \leq \Pi_{a_n}^2 \leq \mathbb{1}, \quad 0 \leq \bar{\Pi}_{b_m}^2 \leq \mathbb{1}; \tag{4-23}$$

where $\mathbb{1}$ is the identity operator. Moreover,

$$\begin{aligned} 0 \leq & \left(\Pi_{a_n} + \bar{\Pi}_{b_m} - \frac{1}{2}\mathbb{1}\right)^2 \\ =& \Pi_{a_n}\bar{\Pi}_{b_m} + \bar{\Pi}_{b_m}\Pi_{a_n} - \frac{1}{4}\mathbb{1} \\ =& 2\Pi_{a_n b_m} + \frac{1}{4}\mathbb{1}, \end{aligned} \tag{4-24}$$

which gives a lower bound for eq. (4-22). To find an upper bound, consider the following

$$\begin{aligned} 0 \leq \left(\Pi_{a_n} + \bar{\Pi}_{b_m}\right)^2 =& \Pi_{a_n}^2 + \bar{\Pi}_{b_m}^2 - 2\Pi_{a_n b_m} \\ \leq& 2 \cdot \mathbb{1} - 2\Pi_{a_n b_m}. \end{aligned} \tag{4-25}$$

Given that $\mathrm{Tr}[\rho_{\mathcal{S}}(0)] = 1$, inequalities (4-24) and (4-25) bound the joint QPDF to obtain outcomes n and m under the Margenau-Hill scheme according to

$$-\frac{1}{8} \leq \mathcal{P}^{MH}(n,m) \leq 1. \tag{4-26}$$

For a more general version of this proof, see theorem 7.5 of [122].

4.3.2. Path integral approach to the Margenau-Hill scheme

Now that we have described the work QPDF for the Margenau-Hill scheme, the corresponding CF can be computed. Replacing equations (4-18) and (4-19) into (3-35) gives the CF of work under the Margenau-Hill scheme

$$\begin{aligned} \chi_w^{MH}(\nu) :=& \int dw \mathcal{P}^{MH}(w) \exp\left(i\nu w\right) \\ =& \sum_{nm} \int dw \mathcal{P}^{MH}(n,m)\delta(w - (E_n^0 - E_m^\tau)) \\ =& \frac{1}{2}\sum_{nm} \left(\mathrm{Tr}\left[\bar{\Pi}_{E_m^\tau}\Pi_{E_n^0}\rho_{\mathcal{S}}(0)\right] + \mathrm{Tr}\left[\Pi_{E_n^0}\bar{\Pi}_{E_m^\tau}\rho_{\mathcal{S}}(0)\right]\right) e^{i\nu(E_m^\tau - E_n^0)}, \end{aligned} \tag{4-27}$$

where I set $\hbar = 1$. Each term in eq. (4-27) corresponds to a two-times correlation function, similar to the CF for the TPM scheme (see eq. (3-37)). Take for instance the term to the

right in eq. (4-27)

$$\begin{aligned}\sum_{nm}\mathrm{Tr}\left[\Pi_{E_n^0}\bar{\Pi}_{E_m^\tau}\rho_{\mathcal{S}}(0)\right]e^{i\nu(E_m^\tau-E_n^0)} =& \sum_{nm}\sum_{n'}\langle E_{n'}^0|E_n^0\rangle\langle E_n^0|U_{\mathcal{S}}^\dagger e^{i\nu E_m^\tau}|E_m^\tau\rangle\langle E_m^\tau|U_{\mathcal{S}}\rho_{\mathcal{S}}(0)e^{-i\nu E_n^0}|E_{n'}^0\rangle \\ =& \sum_{nm}\langle E_n^0|U_{\mathcal{S}}^\dagger e^{i\nu E_m^\tau}|E_m^\tau\rangle\langle E_m^\tau|U_{\mathcal{S}}\rho_{\mathcal{S}}(0)e^{-i\nu E_n^0}|E_n^0\rangle \\ =& \sum_{m}\mathrm{Tr}\left[U_{\mathcal{S}}^\dagger e^{i\nu H_{\mathcal{S}}(\lambda(\tau))}|E_m^\tau\rangle\langle E_m^\tau|U_{\mathcal{S}}\rho_{\mathcal{S}}(0)e^{-i\nu H_{\mathcal{S}}(\lambda(0))}\right] \\ =& \mathrm{Tr}\left[e^{i\nu\bar{H}_{\mathcal{S}}(\lambda(\tau))}\rho_{\mathcal{S}}(0)e^{-i\nu H_{\mathcal{S}}(\lambda(0))}\right]. \end{aligned} \tag{4-28}$$

Following a similar procedure for the term to the left of eq. (4-27), is easy to show that the CF in this case gives [123]

$$\chi_w^{MH}(\nu) = \frac{1}{2}\mathrm{Tr}\left[\left\{e^{i\nu\bar{H}_{\mathcal{S}}(\lambda(\tau))}, e^{-i\nu H_{\mathcal{S}}(\lambda(0))}\right\}\rho_{\mathcal{S}}(0)\right], \tag{4-29}$$

where $\{A,B\} = AB + BA$ represents the anti-commutation operation. Up to this point, it is possible to illustrate how this CF differs from that of the TPM scheme by noting that the initial state does not appear diagonalized as in equation (3-37). Moreover, the effect of this can be elucidated by considering an arbitrary initial state of the form of equation (3-16) and replacing it in (4-29):

$$\rho(0) = \sum_{kl} A_{kl}e^{i\Delta_{kl}}|k\rangle\langle l|, \tag{4-30}$$

$$\begin{aligned}\chi_w^{MH}(\nu) &= \frac{1}{2}\sum_{nm}\left(\mathrm{Tr}\left[\bar{\Pi}_{E_m^\tau}\Pi_{E_n^0}\rho(0)\right] + \mathrm{Tr}\left[\Pi_{E_n^0}\bar{\Pi}_{E_m^\tau}\rho(0)\right]\right)e^{i\nu(E_m^\tau-E_n^0)} \\ &= \frac{1}{2}\sum_{mnn'}\left(A_{nn'}e^{i\Delta_{nn'}}\langle E_{n'}^0|\bar{\Pi}_{E_m^\tau}|E_n^0\rangle + c.c\right)e^{i\nu(E_m^\tau-E_n^0)} \\ &= \sum_{m}\sum_{nn'}\mathrm{Re}\left\{A_{nn'}e^{i\Delta_{nn'}}\langle E_{n'}^0|\bar{\Pi}_{E_m^\tau}|E_n^0\rangle\right\}e^{i\nu(E_m^\tau-E_n^0)}. \end{aligned} \tag{4-31}$$

Considering the diagonal and off-diagonal elements of the inner sum separately the TPM constribution can be distinguished from the coherences contribution:

$$\chi_w^{MH}(\nu) = \chi_w^{TPM}(\nu) + \sum_{m}\sum_{n\neq n'}e^{i\nu(E_m^\tau-E_n^0)}\mathrm{Re}\left\{A_{nn'}e^{i\Delta_{nn'}}\langle E_{n'}^0|\bar{\Pi}_{E_m^\tau}|E_n^0\rangle\right\}, \tag{4-32}$$

showcasing how the MH scheme recovers the TPM scheme for incoherent states.

The objective now is to build the path integral representation of eq. (4-29). For this, note that eq. (4-28) strongly resembles the CF for the TPM scheme (see eq. (4-10)) except for the application of the dephasing operator on the initial density matrix $\rho_{\mathcal{S}}(0)$ in the case of the

TPM scheme. This reflects the fact that the Margenau-Hill scheme allows for the survival of initial coherences beyond the initial time. Moreover, defining

$$f(\nu) := \mathrm{Tr}\left[e^{i\nu\bar{H}_{\mathcal{S}}(\lambda(\tau))}e^{-i\nu H_{\mathcal{S}}(\lambda(0))}\rho_{\mathcal{S}}(0)\right], \tag{4-33}$$

it is easy to show the following symmetry relation

$$f^*(-\nu) = \mathrm{Tr}\left[e^{-i\nu H_{\mathcal{S}}(\lambda(0))}e^{i\nu\bar{H}_{\mathcal{S}}(\lambda(\tau))}\rho_{\mathcal{S}}(0)\right]. \tag{4-34}$$

Thus, the path integral representation of eq. (4-29) can be constructed in close analogy to eq. (3-38) (setting $\hbar = 1$)

$$\begin{aligned}
2\chi_w^{MH}(\nu) =& f(\nu) + f^*(-\nu) \\
=& \int dx_i dy_i dx_f dy_f \delta(x_f - y_f)\rho_0(x_i, y_i) \\
& \left[\int Dx \int Dy^* e^{i\left(S_2^{\nu}[x] - S_2^{\nu}[y]\right)} e^{i\nu W_{\nu}^{TPM}[x]} + \int Dx^* \int Dy e^{-i\left(S_2^{-\nu}[x] - S_2^{-\nu}[y]\right)} e^{i\nu W_{-\nu}^{TPM}[x]}\right] \\
=& \int dx_i dy_i dx_f dy_f \delta(x_f - y_f)\rho_0(x_i, y_i) \\
& \left[\int Dx \int Dy^* e^{i\left(S_2^{\nu}[x] - S_2^{\nu}[y]\right)} e^{i\nu W_{\nu}^{TPM}[x]} + \int Dx^* \int Dy e^{i\left(S_1^{-\nu}[y] - S_1^{-\nu}[x]\right)} e^{-i\nu W_{-\nu}^{TPM}[y]}\right],
\end{aligned} \tag{4-35}$$

where $\rho_0(x_i, y_i) := \langle x_i | \rho_{\mathcal{S}}(0) | y_i \rangle$ was defined. Remember that $S_2^{\nu}[x]$ and $W_{\nu}^{TPM}[x]$ are given by equations (3-40) and (3-41) respectively. From the second to the third equality I used

$$e^{-i\left(S_2^{-\nu}[x] - S_2^{-\nu}[y]\right)} e^{i\nu W_{-\nu}^{TPM}[x]} = e^{i\left(S_1^{-\nu}[y] - S_1^{-\nu}[x]\right)} e^{-i\nu W_{-\nu}^{TPM}[y]}, \tag{4-36}$$

that follows from eq. (B-27). By explicitly writing the actions,

$$S_1^{-\nu}[y] = \int_0^{\tau} dt \mathcal{L}[\lambda(t), y(t-\nu)] - \int_0^{\nu} dt \mathcal{L}[\lambda(0), y(t-\nu)] \tag{4-37}$$

$$S_2^{\nu}[x] = \int_0^{\tau} dt \mathcal{L}[\lambda(t), x(t)] + \int_0^{\nu} dt \mathcal{L}[\lambda(\tau), x(t+\tau)], \tag{4-38}$$

and the work functionals,

$$W_{\nu}^{TPM}[x] = \int_0^{\tau} \frac{dt}{\nu} \int_0^{\nu} dt' \dot{\lambda}(t) \frac{\partial}{\partial \lambda(t)} V[\lambda(t), x(t+t')] \tag{4-39}$$

$$W_{-\nu}^{TPM}[y] = \int_0^{\tau} \frac{dt}{\nu} \int_0^{\nu} dt' \dot{\lambda}(t) \frac{\partial}{\partial \lambda(t)} V[\lambda(t), y(t-t')] \tag{4-40}$$

the symmetry between the two terms of eq. (4-35) becomes clearer. Note that the first set of path integrals in eq. (4-35) corresponds to the contribution to work due to the forward

trajectories with an action given by the difference between similar contributions $S_2^{\nu}[x]$ and $S_2^{\nu}[y]$ of both the forward and the backward trajectories respectively; on the other hand, the second set of path integrals accounts for the contributions to work due to the back action of the reversed backward trajectories, characterized by the difference $S_1^{-\nu}[y] - S_1^{-\nu}[x]$ instead.

From eq. (4-29) it is clear that the contributions of the coherences in the initial state can be distinguished simply by writing

$$\rho_{\mathcal{S}}(0) = \mathcal{D}\left[\rho_{\mathcal{S}}(0)\right] + \mathcal{C}\left[\rho_{\mathcal{S}}(0)\right], \tag{4-41}$$

where $\mathcal{C}[A] := A - \mathcal{D}[A]$ corresponds to the off-diagonal of A. In fact, in 2020 M. García et. al., compared the first two moments of work between the TPM and the Margenau-Hill schemes by means of the C_{l_1} norm (see sec. 3.2.4), finding that, for a closed system undergoing a cyclic process and starting at $\rho_{\mathcal{S}}(0)$, the following inequality holds [38]

$$\left|\mathrm{E}^{MH}[w] - \mathrm{E}^{TPM}[w]\right| \leq \frac{1}{2} C_{l_1}\left(\rho_{\mathcal{S}}(0)\right) \sum_m |E_m^{\tau}|, \tag{4-42}$$

where the moments $\mathrm{E}^{P}[w^k]$ are determined by the corresponding CF for the protocol P by means of eq. (3-35).

A similar analysis of the role of initial coherences in the path integral formulation of the Margenau-Hill scheme (or others) may be achievable by identifying the off-diagonal contributions to $\rho_0(x_i, y_i)$, which can be done by noting that

$$\rho_0(x_i, y_i) = \rho_0^{diag}(x_i, y_i) + \rho_0^{coh}(x_i, y_i), \tag{4-43}$$

where $\rho_0^{diag}(x_i, y_i) = \langle x_i | \mathcal{D}\left[\rho_{\mathcal{S}}(0)\right] | y_i \rangle$ and $\rho_0^{coh}(x_i, y_i) = \langle x_i | \mathcal{C}\left[\rho_{\mathcal{S}}(0)\right] | y_i \rangle$.

In contrast to the approach of [38], the path integral formulation of the Margenau-Hill scheme shows the potential to provide further conceptual insight on the role of coherence due to the possibility to not only distinguish between the contributions quantified by C_{l_1}, but also to explicitly identify and distinguish the back action of trajectories propagating forward and backwards in time, as illustrated by eq. (4-35).

5. Conclusions

The generalization of concepts from phenomenological thermodynamics and quantum stochastic thermodynamics to the quantum regime is not a straightforward task due to the back action that energy measurements have over quantum systems. However, these theories serve as important benchmarks to which quantum thermodynamics should converge in the classical limit (although this only holds for FTPs, according to the no-go theorem presented in sec. 4.2). Chapter 2 provides a compelling introduction to these subjects, building up the conceptual framework needed to tackle the description of thermodynamic processes in quantum setups. The development of the stochastic energetic framework [20] is of particular importance due to the derivation of the classical work definition along single trajectories, given by eq. (2-28), which appears as the first order approximation of the work functional under the path integral approach to the TPM scheme [13] (see eq. (3-42)).

In classical stochastic thermodynamics, fluctuation theorems serve to describe the underlying statistics of important thermodynamic quantities such as work and heat at a microscopic level, showing that there are privileged events that are exponentially more likely than others, which defines what is commonly called the arrow of time. The fluctuation theorem for heat transfer in the transition from an initial microcanonical state to thermalization with a thermal environment presented in sec. 2.4 provides new insights on the the statistics of processes with contrary heat flows in systems undergoing thermalization.

Moving forward to the quantum regime, a heuristic exploration of coherence is presented in sec. 3.2.2, showing a way in which it can be understood as a quantum feature fully characterized by the off-diagonal elements of the density matrix only relying on the phase differences between elements of a fixed basis of the Hilbert space for single particle systems with an arbitrary number of energy levels, which starkly contrasts with the QRT of coherence presented along the remaining of sec. (3.2) and the definition of the C_{l_1} coherence quantifier given by eq. (3-26) [86].

Although the clear limitations of the TPM approach to work in regards to the assessment of the impact that coherences in the initial state may have on thermodynamic processes, this approach has proven to be of fundamental importance to describe the energetics of closed quantum systems under external driving due to the possibility to recover well known results from classical stochastic thermodynamics, like the Tasaki-Crooks quantum fluctuation the-

orem derived in sec. 4.1 by means of the microreversibility principle for a system starting at thermal equilibrium with a canonical environment [14].

Moreover, the TPM scheme serves to define classification criteria for the possible definitions that work may have in the quantum regime in virtue of the no-go theorem developed by Perarnau-Llobet et. al. in [32] and refined by Matteo Lostaglio in [9], where it is shown the intrinsic relation between the appearance of negative probabilities in the distribution of work and strong forms of nonclassicality related to contextuality in operational descriptions of quantum mechanics [29, 110].

The Margenau-Hill scheme described in sec. 4.3 avoids an initial projective measurement of energy by considering a special estimation of the initial Hamiltonian built upon the results of a projective energy measurement at the end of the protocol, enabling the assessment of initial coherent states at the cost of the introduction of negativities in the work distribution [38, 42], which seems to emerge due to the incompatibility between the initial and final Hamiltonian [30]. These estimation procedure seems to be equivalent to performing generalized weak measurements of the initial energy [39, 84].

As is to be expected, the CF of work in the Margenau-Hill scheme reflects the possibility to consider initial coherent states [123] (see eq. (4-29)). Based on the approach to the TPM scheme developed by Ken Funo and H.T. Quan in [13], the path integral formulation of the Margenau-Hill scheme can be built (see sec. 4.3.2). There, a symmetric interplay between the contributions corresponding to forward and backward propagating paths can be identified, contributing to the understanding of the effect of successive measurements of incompatible observables from this perspective and is a step forward towards the definition of a work functional beyond the TPM scheme. Furthermore, these results enable the possibility to study heat in the Margenau-Hill scheme by means of the Feynman-Vernon formalism [124], as has already been done for the TPM scheme [16].

A. Appendix: The non-Markovian Langevin equation for a harmonic bath

Here I show a full derivation for the non-Markovian Langevin equation, corresponding to equation (2-11) in the main text, following references [20, 56].

Consider a particle of mass M immersed in a thermal environment at inverse temperature $\beta = 1/k_B T$ represented by N microscopic oscillating particles of mass m. The Brownian particle is under the effect of an external force described by a potential $V(\lambda_t, q)$ completely parametrized by λ_t, where p is the conjugate momentum to the particle coordinate q. Let the position and momentum of the nth bath oscillator be q_n and p_n respectively, and ω_n be its frequency. The Hamiltonian of the composite system is thus given by:

$$H = \frac{p^2}{2M} + V(\lambda_t, q) + \sum_{n=1}^{N} \frac{p_n^2}{2m} + \sum_{n=1}^{N} \frac{m\omega_n^2}{2} \left(q_n - \frac{\gamma_n}{m\omega_n^2} q \right)^2, \tag{A-1}$$

where γ_n represents the strength of the coupling between the Brownian particle and the nth oscillator [20]. Expanding the last term of (A-1) the identification shown in (2-7) is easily obtained. Remember that the goal is to find the equation of motion for the position of the Brownian particle eliminating its dependency of the environmental degrees of freedom. For this end we can calculate the Hamilton equations of motion from equation (A-1) for both the Brownian particle

$$\dot{q} = \frac{p}{M}, \tag{A-2}$$

$$\dot{p} = -\frac{\partial V(\lambda_t, q)}{\partial q} + \sum_{n=1}^{N} \gamma_n \left(q_n - \frac{\gamma_n}{m\omega_n^2} q \right), \tag{A-3}$$

and the environment

$$\dot{q_n} = \frac{p_n}{m}, \tag{A-4}$$

$$\dot{p_n} = \gamma_n q - m\omega_n^2 q_n. \tag{A-5}$$

Deriving equation (A-4) once with respect to time and using (A-5) results in the inhomogeneous harmonic equation

$$\ddot{q}_n + \omega_n^2 q_n = \frac{\gamma_n}{m} q. \tag{A-6}$$

The general solution to the homogeneous problem is simply given by

$$c_1 \cos(\omega_n t) + c_2 \sin(\omega_n t). \tag{A-7}$$

A particular solution to this equation can be found by means of the variation of parameters technique. Assuming

$$\tilde{q}_n(t) = \tilde{c}_1(t) \cos(\omega_n t) + \tilde{c}_2(t) \sin(\omega_n t), \tag{A-8}$$

where

$$\tilde{c}_1(t) = -\frac{\gamma}{m\omega_n} \int_0^t q(s) \sin(\omega_b s) ds, \quad \tilde{c}_2(t) = \frac{\gamma}{m\omega_n} \int_0^t q(s) \cos(\omega_b s) ds.$$

Using basic trigonometric identities, equation (A-8) simplifies to

$$\tilde{q}_n(t) = \frac{\gamma}{m\omega_n} \int_0^t q(s) \sin(\omega_n (t-s)) ds. \tag{A-9}$$

From a mechanical viewpoint we know that the effect of each particle in the bath is to either push the particle in a certain direction or to slow it down a little bit. The latter can be identified macroscopically as a friction like effect, which is dependent on the velocity of the Brownian particle rather than its position. For this reason, it is convenient to write equation (A-9) in terms of $\dot{q}$ instead of q. This can be achieved integrating by parts [56]

$$\tilde{q}_n(t) = \frac{\gamma}{m\omega_n^2} \left(q(t) - q(0) \cos(\omega_n t) \right) - \frac{\gamma}{m\omega_n^2} \int_0^t \dot{q}(s) \cos(\omega_n (t-s)) ds. \tag{A-10}$$

Summing up equations (A-7) and (A-10) and noting that $c_1 = q_n(0)$ and $c_2 = \dot{q}_n(0)/\omega_n$ we can build the solution for the position of the n-th particle of the bath

$$\begin{aligned} q_n(t) =& \frac{\gamma_n}{m\omega_n^2} q(t) - \frac{\gamma_n}{m\omega_n^2} \int_0^t \dot{q}(s) \cos(\omega_n (t-s)) ds \\ &+ \left(q_n(0) - \frac{\gamma_n}{m\omega_n^2} q(0) \right) \cos(\omega_n t) + \frac{\dot{q}_n(0)}{\omega_n} \sin(\omega_n t) \end{aligned} \tag{A-11}$$

Note that this expression only depends on the initial conditions for the environmental particle, its frequency ω_n and on the position of the Brownian particle as a function of time $q(t)$. Replacing (A-11) into (A-3) yields to the second order integro-differential given by equation (2-11), where $\xi(t)$ is given in terms of the initial positions and momenta of the microscopic particles:

$$\xi(t) := \sum_{n=1}^{N} \left[\gamma_n \left(q_n(0) - \frac{\gamma}{m\omega_n^2} q(0) \right) \cos(\omega_n t) + \frac{\gamma_n \dot{q}_n(0)}{\omega_n} \sin(\omega_n t) \right]. \tag{A-12}$$

Given the large size of the environment, $\xi(t)$ can be regarded as random force depending on the initial conditions of the microscopic particles conforming the environment, which can be sampled from a canonical distribution $P(\{q_n(0), p_n(0)\}) \propto \exp(-\beta H_B(0))$. Since the

Hamiltonian H_B is the sum of the initial energies of the microscopic particles, their position and momentum can be sampled as independent variables following the canonical distribution with energies

$$E_n(0) = \frac{p_n^2(0)}{2m} + \frac{m\omega_n^2 q_n(0)^2}{2},$$

where the initial position of the Brownian particle was chosen as the origin of the reference frame $q(0) = 0$ so that the average of the initial positions and momenta are zero, and their variances

$$\left\langle (q_n(0))^2 \right\rangle = \frac{k_B T}{m\omega_n^2}, \quad \left\langle (p_n(0))^2 \right\rangle = m k_B T.$$

Since the noise $\xi(t)$, given by equation (A-12), is a linear combination of Gaussian variables, it also follows a normal distribution with zero mean and correlation function

$$\langle \xi(t)\xi(t') \rangle = k_B T \zeta(t - t'). \tag{A-13}$$

B. Appendix: The characteristic function of work in the TPM scheme

Following the procedure of [13] a path integral formula for the CF of work in the TPM scheme can be obtained. Representing eq. (3-37) in the positivion representation, the CF can be expressed in terms of contributions from all possible initial and final positions

$$\begin{aligned}\chi_w^{TPM}(\nu) &= \mathrm{Tr}\left[U_{\mathcal{S}} e^{-i\nu H_{\mathcal{S}}(\lambda(0))}\mathcal{D}[\rho_{\mathcal{S}}(0)]U_{\mathcal{S}}^{\dagger} e^{i\nu H_{\mathcal{S}}(\lambda(\tau))}\right] \\ &= \int dx_f dy_f \delta(x_f - y_f)\left\langle x_f\right| U_{\mathcal{S}} e^{-i\nu H_{\mathcal{S}}(\lambda(0))}\mathcal{D}[\rho_{\mathcal{S}}(0)]U_{\mathcal{S}}^{\dagger} e^{i\nu H_{\mathcal{S}}(\tau)}\left|y_f\right\rangle \\ &= \int dx_f dy_f \delta(x_f - y_f)\int dy_i dx_i \left\langle x_f\right| U_{\mathcal{S}} e^{-i\nu H_{\mathcal{S}}(\lambda(0))}\left|x_i\right\rangle \rho_0^{diag}(x_i, y_i)\left\langle y_i\right| U_{\mathcal{S}}^{\dagger} e^{i\nu H_{\mathcal{S}}(\tau)}\left|y_f\right\rangle,\end{aligned} \tag{B-1}$$

where $\rho_0^{diag}(x_i, y_i) := \left\langle x_i\right|\mathcal{D}[\rho_{\mathcal{S}}(0)]\left|y_i\right\rangle$, and the time evolution operator of the system is evaluated as $U_{\mathcal{S}} := U_{\mathcal{S}}(0,\tau)$. Note that the introduction of $\int dx_f dy_f \delta(x_f - y_f)$ accounts for the trace in the first line and $U_{\mathcal{S}} := U_{\mathcal{S}}(0,\tau)$ stands for the time evolution operator between times $t = 0$ and $t = \tau$. The above expression clearly indicates that the CF can be built from contributions of pairs of paths, with one of the paths evolving forward and the other backwards in time.

Consider first the path evolving forward in time corresponding to the first matrix element of (B-1). Introducing an intermediate time $\nu \in [0,\tau]$, and a probing position x_ν corresponding to this time

$$\left\langle x_f\right| U_{\mathcal{S}}(0,\tau) e^{-i\nu H_{\mathcal{S}}(\lambda(0))}\left|x_i\right\rangle = \int dx_\nu \left\langle x_f\right| U_{\mathcal{S}}(0,\tau)\left|x_\nu\right\rangle\left\langle x_\nu\right| e^{-i\nu H_{\mathcal{S}}(\lambda(0))}\left|x_i\right\rangle. \tag{B-2}$$

Note that the corresponding time interval of the time evolution operator in the left factor overlaps with the time interval corresponding to the exponentiated Hamiltonian in the second. A more convenient representation can be achieved with the change of variables $t = t' - \nu$:

$$\begin{aligned}U_{\mathcal{S}}(0,\tau) =& \mathcal{T}\exp\left(-i\int_0^{\tau} dt H_{\mathcal{S}}(\lambda(t))\right) \\ =& \mathcal{T}\exp\left(-i\int_{\nu}^{\tau+\nu} dt' H_{\mathcal{S}}(\lambda(t'-\nu))\right) =: U_{\mathcal{S}}^{+}(\nu,\tau+\nu),\end{aligned} \tag{B-3}$$

where the shifted time evolution operator U^+ is defined. Note that the introduced shift not only affects the integration limits, but also the control parameter λ. Rewriting eq. (B-2) yields

$$\langle x_f| U_{\mathcal{S}}(0,\tau)e^{-i\nu H_{\mathcal{S}}(\lambda(0))} |x_i\rangle = \int dx_\nu \langle x_f| U^+_{\mathcal{S}}(\nu,\tau+\nu) |x_\nu\rangle \langle x_\nu| e^{-i\nu H_{\mathcal{S}}(\lambda(0))} |x_i\rangle . \tag{B-4}$$

The two matrix elements appearing in equation (B-4) now correspond to the time intervals $[\nu,\tau+\nu]$ and $[0,\nu]$ respectively. Applying the multiplicative property of the time evolution operator, i.e.

$$U(t_1,t_3) = U(t_2,t_3)U(t_1,t_2); \quad t_1 < t_2 < t_3,$$

the aforementioned time intervals can be divided in as many smaller intervals as needed, inducing also a partition in the space representation defined by the positions [125]. This way, the shifted time evolution operator in the first matrix element of eq. (B-4) can split into $K+1$ intervals

$$U^+_{\mathcal{S}}(\nu,\tau+\nu) = U^+_{\mathcal{S}}(t_K,\tau+\nu)U^+_{\mathcal{S}}(t_{K-1},t_K)\cdots U^+_{\mathcal{S}}(t_{k-1},t_k)\cdots U^+_{\mathcal{S}}(t_1,t_2)U^+_{\mathcal{S}}(\nu,t_1). \tag{B-5}$$

Similarly, the exponentiated Hamiltonian in the second matrix element of (B-4) can be split into $L+1$ intervals

$$e^{-i\nu H_{\mathcal{S}}(\lambda(0))} = e^{-i(\nu-t'_L)H_{\mathcal{S}}(\lambda(0))}e^{-i(t'_L-t'_{L-1})H_{\mathcal{S}}(\lambda(0))}\cdots e^{-i(t'_l-t'_{l-1})H_{\mathcal{S}}(\lambda(0))}\cdots e^{-i(t'_2-t'_1)H_{\mathcal{S}}(\lambda(0))}e^{-it'_1H_{\mathcal{S}}(\lambda(0))}. \tag{B-6}$$

Inserting the identities $\int dx_k |x_k\rangle\langle x_k|$ and $\int dx_l |x_l\rangle\langle x_l|$ corresponding to the K and L intermediary times introduced before respectively, equation (B-4) can be casted as:

$$\begin{aligned}
&\langle x_f| U_{\mathcal{S}}(0,\tau)e^{-i\nu H_{\mathcal{S}}(\lambda(0))} |x_i\rangle = \\
&\int dx_\nu \int dx_1\cdots dx_K \langle x_f| U^+_{\mathcal{S}}(t_K,\tau+\nu) |x_K\rangle \cdots \langle x_k| U^+_{\mathcal{S}}(t_{k-1},t_k) |x_{k-1}\rangle \cdots \langle x_1| U^+_{\mathcal{S}}(\nu,t_1) |x_\nu\rangle \\
&\int dx'_1\cdots dx'_L \langle x_\nu| e^{-i(\nu-t'_L)H_{\mathcal{S}}(\lambda(0))} |x'_L\rangle \cdots \langle x'_l| e^{-i(t'_l-t'_{l-1})H_{\mathcal{S}}(\lambda(0))} |x'_{l-1}\rangle \cdots \langle x'_1| e^{-it'_1H_{\mathcal{S}}(\lambda(0))} |x_i\rangle
\end{aligned} \tag{B-7}$$

In the limit $K,L\to\infty$, the Hamiltonian on each infinitesimal time interval can be regarded as constant [125].

$$\begin{aligned}
U^+_{\mathcal{S}}(t_{k-1},t_k) &= \mathcal{T}\exp\left(-i\int_{t_{k-1}}^{t_k} dt H_{\mathcal{S}}(\lambda(t-\nu))\right) \\
&= \exp\left(-iH_{\mathcal{S}}(\lambda(\bar{t}_k-\nu))\Delta t\right),
\end{aligned} \tag{B-8}$$

where $\bar{t}_k = (t_k - t_{k-1})/2$ and $\Delta t = t_k - t_{k-1}$. Evaluating the Hamiltonian at a single time serves to remove the time ordering operator in each interval. Replacing the matrix

elements in the first set of integrals of equation (B-7), replacing the Hamiltonian explicitly and recovering the $\hbar$ dependency:

$$\begin{aligned}\langle x_k|\, U_{\mathcal{S}}^{+}(t_{k-1},t_k)\,|x_{k-1}\rangle &= \langle x_k|\exp\left(-\frac{i}{\hbar}H_{\mathcal{S}}(\lambda(\bar{t}_k-\nu)\Delta t)\right)|x_{k-1}\rangle \\ &= \langle x_k|\exp\left(-\frac{i}{\hbar}\left(\frac{P^2}{2M}+V(\lambda(\bar{t}_k-\nu),X)\right)\Delta t\right)|x_{k-1}\rangle \\ &\approx \langle x_k|\exp\left(-\frac{i\Delta t}{\hbar}T\right)|x_{k-1}\rangle\exp\left(-\frac{i\Delta t}{\hbar}V(\lambda(\bar{t}_k-\nu),x_k)\right), \quad \text{(B-9)}\end{aligned}$$

where $T=\frac{P^2}{2M}$ represents the kinetic energy of the system. The approximation from the second to the third line is valid up to order $\mathcal{O}\left(\frac{\alpha^2}{K^2}\right)$ with $\alpha=\frac{i}{\hbar}(\tau-t_\nu)$ (since here $\Delta t=\frac{\tau-t_\nu}{K}$) and the first correction term is proportional to the commutator $\frac{1}{2}[V,T]$ [126]. This term vanishes in the limit $\Delta t\to 0$ ($K\to\infty$) [125]. The integral in the kinetic term can be written as a familiar Gaussian integral inserting an identity in the momentum basis,

$$\begin{aligned}\langle x_k|\exp\left(-\frac{i\Delta t}{\hbar}T\right)|x_{k-1}\rangle &= \int dp\,\langle x_k|p\rangle\,\langle p|\exp\left(-\frac{i\Delta t}{\hbar}\frac{P^2}{2M}\right)|x_{k-1}\rangle \\ &= \frac{1}{2\pi\hbar}\int dp\exp\left(\frac{i}{\hbar}p(x_k-x_{k-1})\right)\exp\left(-\frac{i\Delta t}{\hbar}T\right) \\ &= \sqrt{\frac{M}{2\pi\hbar i\Delta t}}\exp\left(\frac{iM}{2\hbar\Delta t}(x_k-x_{k-1})^2\right), \quad \text{(B-10)}\end{aligned}$$

where the identity $\langle x|p\rangle=\frac{1}{\sqrt{2\pi\hbar}}e^{\frac{i}{\hbar}px}$ was used and the integral was solved using

$$\int_{-\infty}^{\infty}\exp(-ay^2+by)dy=\sqrt{\frac{\pi}{a}}\exp\left(\frac{b^2}{4a}\right),$$

with $a=\frac{i\Delta t}{2M\hbar}$ and $b=\frac{i}{\hbar}(x_k-x_{k-1})$. Replacing eq. (B-10) into (B-9) yields:

$$\langle x_k|\, U_{\mathcal{S}}^{+}(t_{k-1},t_k)\,|x_{k-1}\rangle=\sqrt{\frac{M}{2\pi\hbar i\Delta t}}\exp\left(\frac{i\Delta t}{\hbar}\left(\frac{M}{2\Delta t^2}(x_k-x_{k-1})^2-V(\lambda(\bar{t}-\nu),x_k)\right)\right). \quad \text{(B-11)}$$

Similarly, for the matrix elements in the second set of integrals in equation (B-7)

$$\langle x'_l|\, e^{-\frac{i\Delta t'}{\hbar}H_{\mathcal{S}}(\lambda(0))}\,|x'_{l-1}\rangle=\sqrt{\frac{M}{2\pi\hbar i\Delta t'}}\exp\left(\frac{i\Delta t'}{\hbar}\left(\frac{M}{2\Delta t'^2}(x'_l-x'_{l-1})^2-V(\lambda(0),x'_l)\right)\right). \quad \text{(B-12)}$$

Replacing equations (B-11) and (B-12) into (B-7):

$$\begin{aligned}\langle x_f|\, U_{\mathcal{S}}^{+}(0,\tau)e^{-i\nu H_{\mathcal{S}}(\lambda(0))}\,|x_i\rangle = \lim_{K,L\to\infty}\int dx_\nu \int dx_0\cdots dx_K \int dx_0'\cdots dx_L' \left(\frac{M}{2\pi i\hbar dt}\right)^{\frac{K+L+2}{2}} \\ \exp\left(\frac{i}{\hbar}\sum_k\left(\frac{M}{2\Delta t^2}(x_k-x_{k-1})^2 - V(\lambda(\bar{t}-\nu),x_k)\right)\Delta t\right)\times \\ \exp\left(\frac{i}{\hbar}\sum_l\left(\frac{M}{2\Delta t'^2}(x_l'-x_{l-1}')^2 - V(\lambda(0),x_l')\right)\Delta t'\right) \quad \text{(B-13)}\end{aligned}$$

Note that the summations in both exponentials correspond to Riemann summations when the limit is evaluated [125], e.g.

$$\lim_{K\to\infty}\sum_{k=0}^{K}\left(\frac{M}{2\Delta t^2}(x_k-x_{k-1})^2 - V(\lambda(\bar{t}-\nu),x_k)\right)\Delta t \to \int_\nu^{\tau+\nu} dt\mathcal{L}[\lambda(t-\nu),x] \qquad \text{(B-14)}$$

where $x := x(t)$ represents the path over which the integration is performed and the Langragian of the system is identified as

$$\mathcal{L}\left[\lambda(t),x\right] = \frac{M}{2}\left(\frac{dx}{dt}\right)^2 - V[\lambda(t),x]. \qquad \text{(B-15)}$$

Baring this in mind, equation (B-13) can be cast as a path integral [124, 13]

$$\langle x_f|\, U_{\mathcal{S}}^{+}(0,\tau)e^{-i\nu H_{\mathcal{S}}(\lambda(0))}\,|x_i\rangle = \int Dx \exp\left(\frac{i}{\hbar}\int_\nu^{\tau+\nu} dt\mathcal{L}[\lambda(t-\nu),x(t)]\right)\exp\left(\frac{i}{\hbar}\int_0^{\nu} dt\mathcal{L}[\lambda(0),x(t)]\right) \qquad \text{(B-16)}$$

where the path integration is performed as

$$\int Dx = \lim_{K,L\to\infty}\int dx_\nu \int dx_1\cdots dx_K \int dx_1'\cdots dx_L' \left(\frac{M}{2\pi i\hbar dt}\right)^{\frac{K+L+2}{2}} \qquad \text{(B-17)}$$

A similar procedure can be followed for the path evolving backwards in time in the integral of equation (B-1),

$$\begin{aligned}\langle y_i|\, U_{\mathcal{S}}^{\dagger}e^{i\nu H_{\mathcal{S}}(\tau)}\,|y_f\rangle &= \left(\langle y_f|\, e^{-i\nu H_{\mathcal{S}}(\tau)}U_{\mathcal{S}}\,|y_i\rangle\right)^* \\ &= \int Dy^* \exp\left(-\frac{i}{\hbar}\int_0^{\tau} dt'\mathcal{L}[\lambda(t'),y(t')]\right)\exp\left(-\frac{i}{\hbar}\int_\tau^{\tau+\nu} dt'\mathcal{L}[\lambda(\tau),y(t')]\right)\end{aligned}$$

In this case, the time shift is done over the exponentiated Hamiltonian term rather than on the evolution operator.

Defining the following actions:

$$S[y] := \int_0^{\tau} dt\mathcal{L}[\lambda(t), y(t)], \tag{B-18}$$

$$S_1^{\nu}[x] := \int_{\nu}^{\tau+\nu} dt\mathcal{L}[\lambda(t-\nu), x(t)] + \int_0^{\nu} dt\mathcal{L}[\lambda(0), x(t)], \tag{B-19}$$

$$S_2^{\nu}[y] := S[y] + \int_{\tau}^{\tau+\nu} dt\mathcal{L}[\lambda(\tau), y(t)]; \tag{B-20}$$

the CF of work for the TPM scheme can be written as [13]

$$\chi_w^{TPM}(\nu) := \int dx_i dy_i dx_f dy_f \delta(x_f - y_f) \int Dx \int Dy^* \rho_0^{diag}(x_i, y_i) \exp\left(\frac{i}{\hbar}\left(S_1^{\nu}[x] - S_2^{\nu}[y]\right)\right) \tag{B-21}$$

Remember that the classical functional of work is given by (2-28).

Computing the partial derivative of the action given by equation (B-20) with respect τ yields to a similar expression in the quantum regime:

$$\begin{aligned}\frac{\partial}{\partial\tau}S_2^{\nu}[x] &= \frac{\partial}{\partial\tau}S[x] + \frac{\partial}{\partial\tau}\int_{\tau}^{\tau+\nu} dt'\mathcal{L}[\lambda(\tau), x(t')] \\ &= \mathcal{L}[\lambda(\tau), x(\tau)] + \mathcal{L}[\lambda(\tau), x(\tau+\nu)] - \mathcal{L}[\lambda(\tau), x(\tau)] + \int_{\tau}^{\tau+\nu} dt'\frac{\partial}{\partial\tau}\mathcal{L}[\lambda(\tau), x(t')] \\ &= \mathcal{L}[\lambda(\tau), x(\tau+\nu)] - \frac{\partial}{\partial\tau}\int_0^{\nu} dt' V[\lambda(\tau), x(t'+\tau)].\end{aligned} \tag{B-22}$$

where the Leibniz rule to derive under the integration sign was used,

$$\frac{\partial}{\partial x}\int_{a(x)}^{b(x)} f(x,t)dt = f(x,b(x))\frac{\partial}{\partial x}b(x) - f(x,a(x))\frac{\partial}{\partial x}a(x) + \int_{a(x)}^{b(x)} dt\frac{\partial}{\partial x}f(x,t), \tag{B-23}$$

and the change $t' \to t' + \tau$ was performed in the third line. Note that since the integration limit do not depend on τ anymore, the partial derivation and the integration sign are interchangeable. Applying the fundamental theorem of calculus and the chain rule to the potential inside the integral in equation (B-22)

$$\begin{aligned}V[\lambda(\tau), x(t'+\tau)] &= \int_0^{\tau} dt\frac{\partial}{\partial t}V[\lambda(t), x(t'+t)] \\ &= \int_0^{\tau} dt\dot{\lambda}(t)\frac{\partial}{\partial\lambda(t)}V[\lambda(t), x(t'+t)].\end{aligned} \tag{B-24}$$

Replacing this into (B-22) leads to

$$\frac{\partial}{\partial\tau}S_2^{\nu}[x] = \mathcal{L}[\lambda(\tau), x(\tau+\nu)] - \nu\frac{\partial}{\partial\tau}W_{\nu}^{TPM}[x], \tag{B-25}$$

where the work functional for the TPM scheme is defined as [13]

$$W_\nu^{TPM}[x] := \int_0^\tau \frac{dt}{\nu} \int_0^\nu dt' \dot{\lambda}(t) \frac{\partial}{\partial \lambda(t)} V[\lambda(t), x(t'+t)]. \tag{B-26}$$

Noting that $\frac{\partial}{\partial \tau} S_1^\nu[x] = \mathcal{L}[\lambda(\tau), x(\tau+\nu)]$ and using equation (B-25), the following identity can be proven [13],

$$S_1^\nu[x] - S_2^\nu[x] = \nu W_\nu^{TPM}[x]. \tag{B-27}$$

Thus, equation (B-21) can be rewritten in terms of the quantum work function as

$$\begin{aligned} \chi_w^{TPM}(\nu) := & \int dx_f dy_f \delta(x_f - y_f) \int Dx \int Dy^* \\ & \rho_0^{diag}(x_i, y_i) \exp\left(\frac{i}{\hbar}\left(S_2^\nu[x] - S_2^\nu[y]\right)\right) \exp\left(i\frac{\nu}{\hbar} W_\nu^{TPM}[x]\right). \end{aligned} \tag{B-28}$$

C. Appendix: Quantum microreversibility principle

As in classical mechanics, the laws of motion in quantum systems are invariant under time-reversal transformations. Take for instance the Schrödinger equation (taking $\hbar = 1$)

$$i\partial_t \psi(\mathbf{r}, t) = \left[-\frac{1}{2m}\nabla^2 + V(\mathbf{r}) \right] \psi(\mathbf{r}, t). \tag{C-1}$$

Consider the change $t \to -t$ and take the complex conjugate of both sides

$$i\partial_t \psi^*(\mathbf{r}, -t) = \left[-\frac{1}{2m}\nabla^2 + V(\mathbf{r}) \right] \psi^*(\mathbf{r}, -t). \tag{C-2}$$

By comparing (C-1) and (C-2) one notes that $\psi_{rev}(\mathbf{r},\mathbf{t}) = \psi^*(\mathbf{r}, -t)$ is a solution of the Schrödinger equation as well, meaning that it is invariant under time reversal transformations just as Newton's laws of movement.

Just as in the classical case, time-reversion in quantum mechanics implies a change in the sign of momentum; this property leads to the commutation relations that defines the time-reversal operator (TRO). Consider for instance a spinless particle and define the TRO Θ as an operator that transforms the position operator $\mathbf{r}$ into $\mathbf{r}$ and the momentum operator $\mathbf{p}$ into $-\mathbf{p}$, such that

$$\Theta \mathbf{r} \Theta^\dagger = \mathbf{r}, \quad \Theta \mathbf{p} \Theta^\dagger = -\mathbf{p}. \tag{C-3}$$

Since $\mathbf{p}$ is a pure imaginary operator, the TRO must satisfy that $\Theta i = -i\Theta$. Therefore, it must be an anti-unitary operator. In the simple case of a spinless particle, the TRO corresponds to the complex conjugate operator $K = K^\dagger$ [104]. From the definition of angular momentum it is easily shown that

$$\Theta \mathbf{L} \Theta^\dagger = -\mathbf{L}, \tag{C-4}$$

which means that Θ anti-commutes with angular momentum operators and in consequence commutes with rotation operators [104]. Since the spin is a particular angular momentum, it must transform anti-unitarily under time reversal transformations.

If we consider now a particle with spin $\mathbf{s}$, the TRO must satisfy

$$\Theta \mathbf{s} \Theta^\dagger = -s, \tag{C-5}$$

such that (C-4) holds for the total angular momentum $\mathbf{J}$. Remembering that the spin components in a basis $\{|s_z,\uparrow\rangle, |s_z,\downarrow\rangle\}$ are given by the Pauli matrices and that the only imaginary matrix is σ_y, it can be shown that the spin components s_i with $i = x, y, z$ satisfy

$$Ks_xK = s_x, \quad Ks_yK = -s_y, \quad Ks_zK = s_z. \tag{C-6}$$

Note that, up to this point, the complex conjugate operator does not anti-commute with every component of the spin $\mathbf{s}$. Therefore, it cannot be the TRO for spin particles. This problem can be addressed by finding an operator T such that $\Theta = TK$ (remember that Θ must satisfy (C-3) and (C-4) for any angular momentum).Then $T = \Theta K$ and $T^\dagger = K\Theta^\dagger$. Multiplying the relations in (C-6) by Θ from the left and by $\Theta^\dagger$ from the right and using equation (C-4), it is easily shown that

$$Ts_xT^\dagger = -s_x, \quad Ts_yT^\dagger = s_y, \quad Ts_zT^\dagger = -s_z, \tag{C-7}$$

and for the configuration coordinates

$$T\mathbf{r}T^\dagger = \mathbf{r}, \quad T\mathbf{p}T^\dagger = -\mathbf{p}. \tag{C-8}$$

Equations (C-7) and (C-8) correspond to the transformation of variables $\mathbf{r}$, $\mathbf{p}$ and $\mathbf{s}$ given by a rotation of the spin alone through an angle π about the y axis $Y_\mathbf{s} = e^{-\pi s_y}$. Summarizing, the complete TRO for a particle with spin $\mathbf{s}$ is specified by[104]

$$\Theta = Y_\mathbf{s}K, \tag{C-9}$$

that for the case of a 1/2 spin particle reduces to

$$\Theta = -i\sigma_yK. \tag{C-10}$$

Using the above description of the TRO, the problem of of quantum microreversibility can be addressed. Consider a closed quantum system described by the time dependent Hamiltonian $H(\lambda(t))$, where $\lambda(t)$ is a time evolution protocol driving the system. The objective is to find a way to relate the quantum trajectories given by the forward evolution protocol $\lambda(t)$ and the initial thermal state in terms of the backward protocol $\tilde{\lambda}(t) = \lambda(\tau - t)$ and the final state of the system. This can be done by discretizing time in the interval $[0, \tau]$ and writing the time evolution operator $U(0, t; \tilde{\lambda})$ as a time ordered product for the backward protocol [14]

$$U(0, \tau - t; \tilde{\lambda}) = \lim_{N\to\infty} e^{-iH(\tilde{\lambda}(\tau - N\epsilon))\epsilon} \cdots e^{-iH(\tilde{\lambda}(0))\epsilon}, \tag{C-11}$$

where $\epsilon = t/N$ denotes the time step. Multiplying by $\Theta^\dagger$ from the left and by Θ from the right, using the fact that Θ must be an anti-unitary operator (i.e. $\Theta i = -i\Theta$ and $\Theta\Theta^\dagger = 1$) and assuming that the Hamiltonian commutes with Θ at all times ($[H, \Theta] = 0$)

$$\begin{aligned}
\Theta^\dagger U(0, \tau - t; \tilde{\lambda})\Theta &= \lim_{N\to\infty} \Theta^\dagger e^{-iH(\lambda(N\epsilon))\epsilon}\Theta\Theta^\dagger e^{-iH(\lambda(N\epsilon+\epsilon))\epsilon} \cdots \Theta\Theta^\dagger e^{-iH(\lambda(\tau-\epsilon))\epsilon}\Theta\Theta^\dagger e^{-iH(\lambda(\tau))\epsilon}\Theta \\
&= \lim_{N\to\infty} e^{iH(\lambda(N\epsilon))\epsilon} e^{iH(\lambda(N\epsilon+\epsilon))} \cdots e^{iH(\lambda(\tau))\epsilon} \\
&= \lim_{N\to\infty} \left[e^{-iH(\lambda(\tau))\epsilon} \cdots e^{-iH(\lambda(N\epsilon+\epsilon))} e^{-iH(\lambda(N\epsilon))\epsilon}\right]^\dagger \\
&= U(t, \tau; \lambda)^\dagger = U(\tau, t; \lambda).
\end{aligned} \tag{C-12}$$

Rewriting the evolution operator on the right hand side as

$$U(\tau, t; \lambda) = U(0, t; \lambda)U(\tau, 0; \lambda) = U(0, t; \lambda)U(0, \tau; \lambda)^{\dagger}, \tag{C-13}$$

equation (C-12) can be casted as

$$U(0, t; \lambda) = \Theta^{\dagger}U(0, \tau - t; \tilde{\lambda})\Theta U(0, \tau; \lambda). \tag{C-14}$$

Equation (C-14) corresponds to the quantum version of the MRP in terms of the time evolution operator. This can be seen by applying this evolution operator to an initial pure state $|i\rangle$ and multiplying by Θ from the left

$$\Theta U(0, t; \lambda)\,|i\rangle = U(0, \tau - t; \tilde{\lambda})\Theta U(0, \tau; \lambda)\,|i\rangle\,, \tag{C-15}$$

which can be written in terms of the final state, as $|f\rangle = U(0, \tau; \lambda)\,|i\rangle$,

$$\Theta\,|\psi_t\rangle = U(0, \tau - t; \tilde{\lambda})\Theta\,|f\rangle\,, \tag{C-16}$$

where I defined $|\psi_t\rangle = U(0, t; \lambda)\,|i\rangle$. Note that equation (C-16) describes the inverted evolution of the state $|\psi_t\rangle$ starting from the final state $|f\rangle$ rather than from the initial state $|i\rangle$ and properly inverting momentum due to the action of the TRO, thus describing the backward evolution of the system.

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