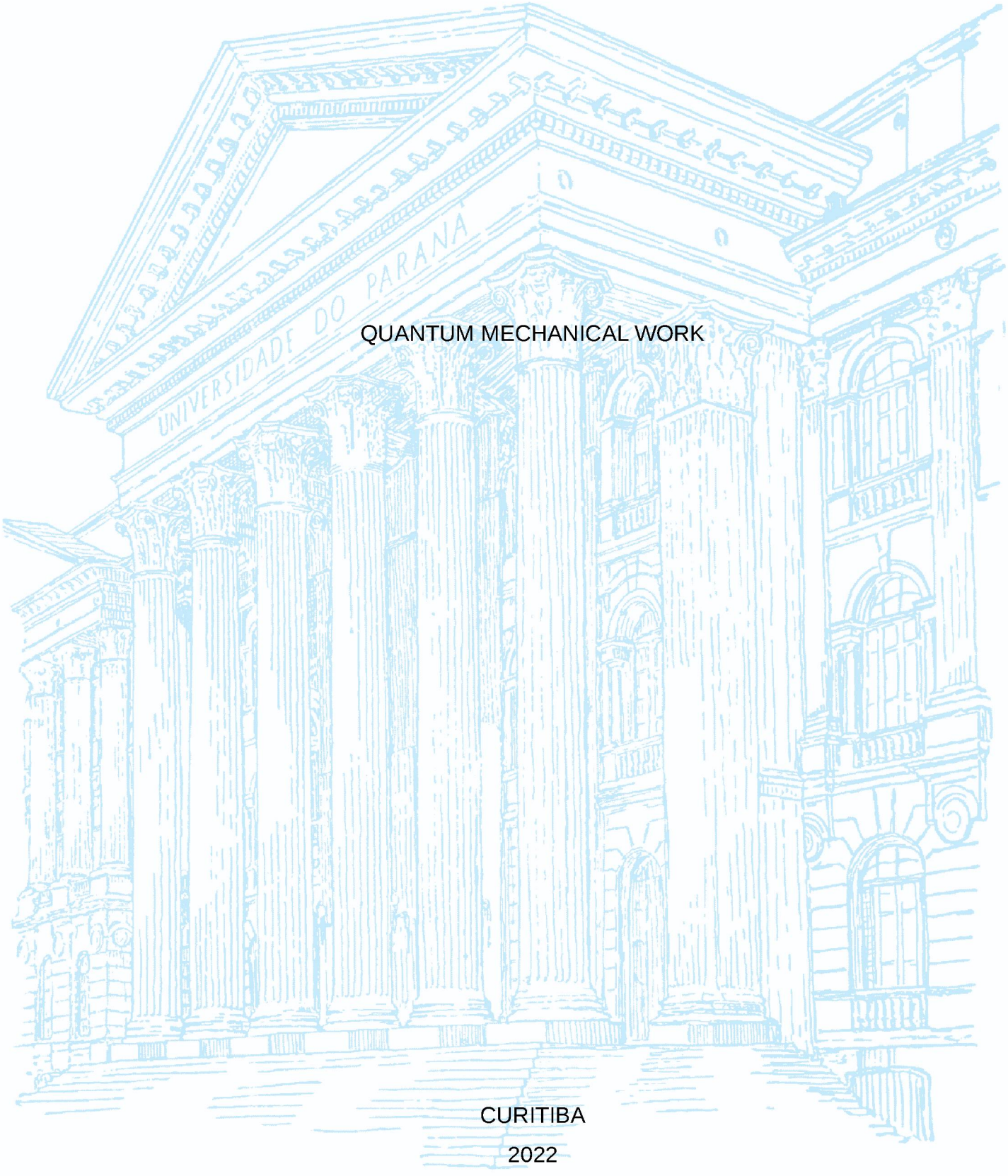
UNIVERSIDADE FEDERAL DO PARANÁ

THALES AUGUSTO BARBOSA PINTO SILVA



QUANTUM MECHANICAL WORK

CURITIBA

2022

THALES AUGUSTO BARBOSA PINTO SILVA

QUANTUM MECHANICAL WORK

Tese apresentada ao Programa de Pós-Graduação em Física do Setor de Ciências Exatas da Universidade Federal do Paraná, como requisito parcial à obtenção do título de Doutor em Física.

Orientador: Prof. Dr. Renato Moreira Angelo

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“If physical theories were people, thermodynamics would be the village witch.”
John Goold, Marcus Huber, Arnau Riera, Lídia del Rio, and Paul Skrzypczyk

RESUMO

Considerado um dos conceitos mais fundamentais da mecânica clássica e da termodinâmica, trabalho tem recebido definições bem fundamentadas no âmbito quântico desde a década de 1970, sendo aplicado com sucesso em diversos contextos. Estudos recentes sobre o conceito ocorreram na área emergente da termodinâmica quântica, onde trabalho é frequentemente caracterizado como uma variável estocástica. Apesar desse notável progresso, ainda é discutível se alguma noção sensível de trabalho e uma forma consistente de levantar suas estatísticas podem ser postas para um cenário estritamente quântico envolvendo um sistema de poucas partículas preparado em estado puro e abandonado à sua dinâmica autônoma fechada. Ao tratar trabalho como um observável da mecânica quântica com um limite clássico bem definido, mostramos aqui que esse cenário pode ser satisfatoriamente materializado. Provamos, a partir de exemplos explícitos, que é possível atribuir autoestados a operadores de trabalho, abrindo caminho para estruturas envolvendo superposição quântica e direcionamento não local de trabalho. Por mais sutil que seja, nossa noção de trabalho da mecânica quântica é experimentalmente testável permitindo levantar suas estatísticas e requer uma atualização de nossa intuição em relação ao conceito de elementos da realidade em dois tempos. Nessa direção, também derivamos uma relação de incerteza entre trabalho e energia, calculamos perturbações energéticas induzidas por medições e ilustramos como a conservação de energia surge como um elemento da realidade física. Além disso, abordamos cenários situados na interface entre termodinâmica e mecânica, nos quais mostramos como estados não triviais e correlacionados podem induzir diferentes relações de flutuação de trabalho e como uma noção útil e rastreável de trabalho, semelhante à descrição da física estatística, pode emergir em um cenário autônomo quântico. Esperamos que, em curto prazo, nossos resultados possam ser testados experimentalmente em plataformas de íons aprisionados e contribuam para um entendimento mais profundo da noção de trabalho em regime quântico e eventualmente termodinâmico.

Palavras-chave: Trabalho. Estatísticas de trabalho. Conservação de energia. Relações de flutuação. Medições quânticas.

ABSTRACT

Regarded as one of the most fundamental concepts of classical mechanics and thermodynamics, work has received well-grounded definitions within the quantum framework since the 1970s, having being successfully applied to many contexts. Recent developments on the concept have taken place in the emergent field of quantum thermodynamics, where work is frequently characterized as a stochastic variable. Notwithstanding this remarkable progress, it is still debatable whether some sensible notion of work and a consistent form of raising its statistics can be posed for a strictly quantum instance involving a few-particle system prepared in a pure state and abandoned to its closed autonomous dynamics. By treating work as a quantum mechanical observable with a well defined classical limit, here we show that this scenario can be satisfactorily materialized. We prove, by explicit examples, that one can indeed assign eigensystems to work operators, paving the way for frameworks involving quantum superposition and nonlocal steering of work. However subtle it may be, our quantum mechanical notion of work is experimentally testable enabling one to raise its statistics and requires an updating of our intuition regarding the concept of two-time elements of reality. In this direction, we also derive a work-energy uncertainty relation, compute the energetic disturbance induced by measurements, and illustrate how energy conservation emerges as an element of physical reality. Moreover, we approached scenarios lying in the interface between thermodynamics and mechanics, in which we show how non-trivial, correlated states may induce different work fluctuation relations and how a useful, traceable notion of work, similar to the statistical-physics description, can emerge in a quantum autonomous scenario. We hope that, in short term, our results can be experimentally tested in trapped-ion platforms and contribute to deepen the understanding of the notion of work in the quantum regime and, eventually, in the thermodynamic one as well.

Keywords: Work. Work statistics. Energy conservation. Fluctuation relations. Quantum measurements.

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1 Introduction

The importance of the physical concept of work to technology and science can hardly be overestimated. From an industrial perspective, work has long been a central concept to the design of heat engines [1, 2] and has recently expanded its range of application to accomplish feats previously unthinkable. For instance, work was crucial for the description of the free energy of RNA molecules [3] as well as to thermodynamically describe not only solar energy systems [4] but also batteries assisted by cooper pair tunneling [5]. Furthermore, work has been regarded in the context of computation [6] and, remarkably, it lies at the core of a study on the transition from inanimate to living matter [7].

From a theoretical standpoint, work covers several different areas of physics. Perhaps its most elementary notion comes from classical mechanics, being intricately connected to the law of conservation of energy. In this context, the newtonian fundamental law of motion, $m_i\ddot{\mathbf{r}}_i = \sum_j \mathbf{f}_{j\to i}$, for a point particle of mass m_i at the position $\mathbf{r}_i$ submitted to conservative forces $\mathbf{f}_{j\to i} = -\nabla_i \mathcal{V}_{ij}$, where $\mathcal{V}_{ij} = \mathcal{V}_{ij}(|\mathbf{r}_i - \mathbf{r}_j|) = \mathcal{V}_{ji}$, can be expressed in terms of energetic terms that are, so to speak, "nonlocal in time", namely,

$$\mathcal{K}_i(t_2) - \mathcal{K}_i(t_1) = \sum_j \mathcal{W}_{j\to i}(t_2, t_1), \tag{1.1}$$

where we defined the kinetic energy $\mathcal{K}_i(t) = m_i\dot{\mathbf{r}}_i^2/2$ and

$$\mathcal{W}_{j\to i}(t_2, t_1) = \int_{t_1}^{t_2} dt\, \dot{\mathbf{r}}_i \cdot \mathbf{f}_{j\to i} = -\int_{t_1}^{t_2} dt\, \dot{\mathbf{r}}_i \cdot \nabla_i \mathcal{V}_{ij}. \tag{1.2}$$

The latter expression defines the mechanical work that particle j does on particle i in the time interval $[t_1, t_2]$ by means of the force $\mathbf{f}_{j\to i}$. In addition to providing a useful rephrasing of Newton's second law along a given segment of a configuration space trajectory, the notion of work paves the way for a sensible statement of the law of conservation of energy. In its general form, the principle reads [8–10]

$$\Delta\mathcal{E}_{\mathrm{S}} = \mathcal{W}_{\mathrm{E}\to\mathrm{S}}, \tag{1.3}$$

where E stands for "the environment" and $\mathcal{E}_{\mathrm{S}}$ for the total energy of "the system S" (the boundary between them being arbitrary and abstract). Clearly, the system energy is conserved only in the absence of external work. In the model discussed above we have $\mathrm{S} = \{i\}$ and $\mathrm{E} = \mathrm{U} - \mathrm{S}$, where U denotes the universe set encompassing all particles, so that $\mathcal{E}_{\mathrm{S}} = \mathcal{K}_i$ and $\mathcal{W}_{\mathrm{E}\to\mathrm{S}} = \sum_{j\in\mathrm{E}} \mathcal{W}_{j\to i} = \int_{t_1}^{t_2} dt\, m_i\, \dot{\mathbf{r}}_i \cdot \ddot{\mathbf{r}}_i$. When S is a many-particle system, the scenario becomes subtler and many definitions of work and related energy changes are admissible even in purely mechanical contexts involving matter systems [11, 12].

As the focus moves onto huge, messy, and hot systems, detailed microscopic aspects of the dynamics often become superfluous. In this domain, a proper account for the balance

of energy is provided by thermodynamics [13–15], a phenomenological theory of smooth thermal processes. Supported by the microscopically oriented formalism of statistical physics [16–18], thermodynamics brings into play for the conservation of energy the notion of heat and defines work in terms of changes of macroscopic degrees of freedom, as for instance the position of a piston, thus implementing the idea that work is the energy transferred to a given system through a *controlled* or *useful* process.

Due to the success of thermodynamics, its extension to more general scenarios, including mesoscopic systems, has been sought. In this context, the area of stochastic thermodynamics flourished, where further adaptations of the notion of work were introduced [19, 20] devoted to smaller systems subjected to non-negligible fluctuations. In this scenario, some acclaimed *work fluctuation theorems* [21–24] were deduced, connecting the stochastic, non-equilibrium character of work to macroscopic features of equilibrium.

Now, how about a genuine quantum mechanical formulation of work? Given the lack of the concept of trajectory in the quantum orthodoxy, which then precludes one from trying a definition such as (1.2), one might think at first that any attempt along these lines would be doomed to failure. Despite these difficulties, some interesting developments have been achieved with use of the Heisenberg picture of mechanical systems [25], and, with more intensive efforts, in the emerging field of quantum thermodynamics [26, 27]. In fact, the first attempts to define work in the quantum domain date back to the 1970s (see, e.g., [23, 28]), and they were devoted to implementing the quasi-equilibrium thermodynamic view of work, in analogy to the stochastic thermodynamics scenarios. These models express the system energy as a Hamiltonian operator $H(\lambda)$ that explicitly depends on a deterministic time-dependent parameter $\lambda(t)$ whose dynamics is imposed by an external macroscopic mechanism, so that work is computed as [19, 21, 28–38]

$$W(t_2, t_1) = \int_{t_1}^{t_2} \langle \partial_t H \rangle \, dt = \int_{t_1}^{t_2} \langle \partial_\lambda H \rangle \, \dot{\lambda} \, dt. \tag{1.4}$$

In full consonance with the definition of work encountered in statistical physics and stochastic thermodynamics [20, 21, 39, 40], this formulation is supplemented with a clear recipe for the derivation of a time-dependent Hamiltonian from a closed autonomous dynamics: after tracing out the degrees of freedom external to a system of interest S, one can obtain master equations of the type [26, 41]

$$\partial_t \rho_{\mathrm{S}} = \frac{[H_u, \rho_{\mathrm{S}}]}{i\hbar} + \mathcal{D}\rho_{\mathrm{S}}, \tag{1.5}$$

where $H_u(t)$ is the operator responsible for the unitary part of the evolution and the superoperator $\mathcal{D}$ is the so-called dissipator, which acts in the reduced state $\rho_{\mathcal{S}}$ of the system of interest. Work is then computed in a similar form as in Eq. (1.4), but considering only H_u [42–44], i.e.,

$$W = \int \mathrm{Tr}_{\mathrm{S}} \left(\rho_{\mathrm{S}} \partial_t H_u \right) dt = \int \langle \partial_t H_u \rangle dt. \tag{1.6}$$

Heat, on the other hand, is connected with the dissipator:

$$Q = \int \mathrm{Tr}_{\mathcal{S}} \left(\partial_t \rho_{\mathcal{S}} H_u\right) dt = \int \mathrm{Tr}_{\mathcal{S}} \left(H_u \mathcal{D} \rho_{\mathcal{S}}\right) dt. \tag{1.7}$$

An important drawback is that this scheme is technically complicated for general strong-coupling regimes. Also, the physical significance of definition (1.4) has recently been questioned, since a Hamiltonian like $H(t) + g\mathbb{1}$, with an arbitrary real function $g = g(t)$, generates a g-independent dynamics but a g-dependent amount of work [32, 45–51]. For sure, this cannot be the case in general. Another point under dispute around definition (1.4) is inherited from the classical analogue; it concerns the issue of whether interaction terms are to be regarded as part of the internal energy of the system, therefore triggering the debate on the notions of *inclusive* and *exclusive* works[1] [45].

There are many other routes to the definition of thermodynamic work in quantum regime, among which we refer the reader to Chapter 2 of the present thesis and references [5, 7, 52–59]. In contrast, the literature still lacks a proper account for the definition of work in genuine quantum *mechanical* scenarios. Incidentally, it is clear that the knowledge accumulated so far, however useful it may be in the thermodynamics context, does not apply to scenarios with correlated, microscopic few-particle systems. Consider, for example, a particle of mass m (the system, S) prepared in a pure state and submitted to some external influence (the environment, E) described by a harmonic potential $V(X) = kX^2/2$. Since the quantum dynamics is determined by the parameter-free Hamiltonian[2] $H = P^2/2m + kX^2/2$, a direct application of equation (1.4) would give $\partial_\lambda (P^2/2m) = 0$ and hence no work at all. This is, however, unexpected because the average kinetic energy of the particle surely varies over time. As a second example, let us take an isolated quantum system composed of two spinless particles. Let $H = P_1^2/2m_1 + P_2^2/2m_2 + V_{12}(|X_1 - X_2|)$ be the Hamiltonian governing the autonomous dynamics, and let ρ be a correlated joint state without any connection *a priori* with equilibrium states[3]. Even if one is able to derive a master equation for an arbitrary-strength potential V_{12} and eventually find an effective driving parameter $\lambda(t)$, the resulting effective Hamiltonian for the reduced dynamics will not be free from the issue of encompassing part of the coupling and, as consequence, the work (1.4) will be submitted to the inclusive-versus-exclusive polemic. In addition, this approach does not shed light on the fundamental question of whether work can be treated as an observable [21, 30, 31, 37, 57, 60–65] and how one can measure it.

Taking these difficulties into account, we propose in this thesis a "bottom-up" perspective to describe work. Instead of starting with a thermodynamic view of work and then trying to extend it to more general cases in the quantum world, we start from an essentially quantum *mechanical* definition of work and only then, by adding specific thermodynamic ingredients to it, we can reach scenarios closer to thermodynamics. This approach aims to respect one

[1] For a more detailed discussion, we refer the reader to Section 2.3.

[2] In the case under scrutiny, k is constant throughout time.

[3] For instance, Gibbs (Canonical), Microcanonical, and Grand Canonical states [40].

of the postulates of quantum mechanics, according to which physical quantities must receive a Hermitian operator in the quantum formalism.

Following this strategy, we first introduce a genuine quantum mechanical (QM) notion of work, by which we mean a concept applicable even to the problem of a single quantum particle prepared in a pure state and submitted to a scalar time-independent potential. We show that QM work can be taken as an observable and prove, by explicit examples, that one can indeed assign eigensystems to work operators and raise its statistics, adding another point of view to the ongoing debate of work distributions in the literature [21, 37, 66–71]. Moreover, we show that an observable-based view of work also paves the way for: (i) frameworks involving quantum superposition and nonlocal steering of work, (ii) the derivation a work-energy uncertainty relations and (iii) the emergence of energy conservation as an element of physical reality.

We also demonstrate how the QM work definition and its indexed notion of internal energy variation can be used to propose a new characterization of measurement-induced energy disturbance. In our approach, we explicitly include the measurement apparatus in the dynamical description in a form, to our knowledge, not yet accounted for in the vast and interesting literature on the theme [59, 72–86].

Next, we move the perspective "upwards", exploring scenarios that lie at the interface between mechanics and thermodynamics. We first analyze in detail how the exponential term $\langle \mathrm{e}^{-\beta_{\mathrm{S}} W_{\mathrm{E}\to\mathrm{S}}} \rangle$, intricately connected to classical fluctuation theorems [21–24, 45, 46, 87–89], changes when nontrivial states (in both classical and quantum realms) are considered for the environment E, a theme still under active debate in the literature [21, 37, 64, 66–68]. Finally, we show how a useful quantum work, a concept inspired by the Statistical Physics, can still emerge from the QM definition, extending the notion of “external variable” or “classic protocol” [19, 21] so as to cover autonomous systems. Additionally, we show that this definition converges to (1.4) at a specific limit.

This thesis is structured as follows: first, we present, in the next chapter, the central difficulties regarding the definition of thermodynamic and/or mechanical work for general systems (quantum and classical); also, some of the main problems and concepts to be considered in later chapters are presented to formally contextualize the reader. Then, our results are described in two distinct parts: one containing the definition of QM work and its main properties and the other devoted to scenarios closer to thermodynamics. The first part is exposed in the following sequence:

- In Chapter 3, we properly define the QM work, its statistical description and the main consequences of describing work as a quantum observable;
- The conservation law of energy and the role of measurements and their induced energetic disturbance are then discussed in Chapter 4;

- To close the first part, we address in Chapter 5 some interesting mathematical features of QM work and possible research directions for the near future.

The second part of the thesis is then exposed in the following order:

- We carry out an investigation of the average $\left\langle \mathrm{e}^{-\beta_{\mathrm{S}} W_{\mathrm{E}\to\mathrm{S}}} \right\rangle$ for a specific system, in both classical and quantum contexts, in Chapter 6; there, we explore various initial preparations, identifying thermal, inertial, correlation, and coherence effects;
- We define, in Chapter 7, what we call the ϵ-Fluctuating Variable, a generalization of the well-known “classical protocols", and present our definition of useful QM work, showing how a notion of trackable work can emerge in systems of few autonomous particles and converge to usual thermodynamics definitions in specific regimes.

Chapter 8 then closes the thesis with our concluding remarks and proposals for future research.

2 Literature review and goals

We review here the theoretical tools needed to support the results presented in later chapters. In addition, we formally enunciate the main problems we intend to solve.

We begin our analysis by presenting relevant aspects regarding the definition of work in Classical Mechanics in Section 2.1, thus introducing the issues to be analyzed in the quantum framework in the next chapter. The thermodynamics notion of work is then addressed in Section 2.2, with the discussion being conducted in the context of equilibrium thermodynamics and statistical physics (large, many-particle, weakly coupled systems) and, afterwards, in the arena of stochastic thermodynamics (small, few-particle, possibly strongly coupled, far from equilibrium systems). Concomitantly, some important results of practical and theoretical interest that surround the concept of work are presented. In Sections 2.3 and 2.4, we expose some obstacles on extending the classic definitions presented to more general scenarios.

In Section 2.5, we analyze the concept of work for both non-autonomous (time-dependent hamiltonian) and autonomous (time-independent hamiltonian) quantum scenarios, punctuating ambiguities in these definitions. Moreover, we discuss the difficulties of statistically describing and experimentally accessing work in the quantum context. Some important bounds on thermodynamics work are then derived in Section 2.6.

A brief discussion of the role of measurement in the energetic balance of a quantum-mechanical system is given in Section 2.7. Then, we review the idea of physical reality in Section 2.8 and discuss its extension to two-time physical quantities.

Finally, at the end of this chapter, we summarily describe the main ideas reviewed throughout the chapter and detail the objectives of this thesis.

2.1 Mechanical work

The definition of work coming from Classical Mechanics is accepted as clear, operational and well-established [8–10]. Given a force field $\mathbf{f}$ applied on a system that executes a displacement $d\mathbf{x}$ on a curve C, work $\mathcal{W}$ is simply defined as

$$\mathcal{W} = \int_C \mathbf{f} \cdot d\mathbf{x}. \tag{2.1}$$

One of the main consequences of the definition (2.1) is that it allows us to clearly identify the internal energy in systems of structureless particles. From now on, we confine our analysis to one-dimensional motion, for the sake of simplicity. Consider the Hamiltonian function

$$\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + \sum_{j>i=1}^{N} \mathcal{V}_{ij}, \tag{2.2}$$

with $\mathcal{V}_{ij} \equiv \mathcal{V}_{ij}(|x_i - x_j|)$. The notation is such that the second parcel above encompasses summations over i and $j > i$. Assume, for a while, that $N = 3$ and select particle 2 as the system of interest S, so that the environment E is composed of particles 1 and 3. In this case, work done by particle j on i is computed, taking the chain rule with respect to time into account, as $\mathcal{W}_{j\to i}(t_2, t_1) = -\int_{t_1}^{t_2} dt\, \dot{x}_i\, \partial_{x_i} \mathcal{V}_{ij}$ so that we find

$$\begin{aligned} \mathcal{W}_{\mathrm{E}\to\mathrm{S}}(t_2, t_1) &\equiv \mathcal{W}_{1\to 2}(t_2, t_1) + \mathcal{W}_{3\to 2}(t_2, t_1) = \int_{t_1}^{t_2} dt\, \dot{x}_2\, m\ddot{x}_2 \\ &= \mathcal{K}_2(t_2) - \mathcal{K}_2(t_1) \equiv \Delta\mathcal{E}_{\mathrm{S}}. \end{aligned} \tag{2.3}$$

where $\Delta\mathcal{E}_{\mathrm{S}} = \Delta\mathcal{K}_2$ is the change in kinetic energy of particle 2 over the interval $[t_1, t_2]$. Thus, departing from the (unambiguous) notion of external work $\mathcal{W}_{\mathrm{E}\to\mathrm{S}}$, we arrive at the notion of internal energy $\mathcal{E}_{\mathrm{S}}$, which here is the kinetic energy of S. Notice that the interaction terms $\mathcal{V}_{12}$ and $\mathcal{V}_{23}$ do not contribute to the internal energy. This is reasonable because they do not even exist when the particle 2 is left alone, so they cannot be "internal".

Let us now redefine the abstract boundary between system and environment: $\mathrm{S} = \{1, 2\}$ and $\mathrm{E} = \{3\}$. By using the identity $\frac{d}{dt}(\mathcal{K}_1 + \mathcal{K}_2 + \mathcal{V}_{12}) = -\dot{x}_1\partial_{x_1}\mathcal{V}_{13} - \dot{x}_2\partial_{x_2}\mathcal{V}_{23}$ and regarding once again $\mathcal{W}_{j\to i}(t_2, t_1) = -\int_{t_1}^{t_2} dt\, \dot{x}_i\, \partial_{x_i}\mathcal{V}_{ij}$, one shows that

$$\mathcal{W}_{\mathrm{E}\to\mathrm{S}}(t_2, t_1) \equiv \mathcal{W}_{3\to 1}(t_2, t_1) + \mathcal{W}_{3\to 2}(t_2, t_1) = \Delta\Big(\mathcal{K}_1 + \mathcal{K}_2 + \mathcal{V}_{12}\Big) \equiv \Delta\mathcal{E}_{\mathrm{S}}. \tag{2.4}$$

Again, the result is intuitive: the internal energy $\mathcal{E}_{\mathrm{S}} = \mathcal{K}_1 + \mathcal{K}_2 + \mathcal{V}_{12}$ now includes the interaction $\mathcal{V}_{12}$ taking place inside the boundary that defines the system. Naturally, the interaction terms $\mathcal{V}_{13}$ and $\mathcal{V}_{23}$ are not part of the internal energy, since they cannot exist in the system $\mathrm{S} = \{1, 2\}$ alone. Here is the point we want to emphasize: once the mechanical work is properly defined, the notion of internal energy emerges automatically. Indeed, when a system is isolated, only the characteristics, and therefore the energy, that essentially belong to that system must survive. The extension to arbitrary N is straightforward. Indeed, for $\mathrm{S} = \{1, 2, \cdots, M\}$ and $\mathrm{E} = \{M+1, M+2, \cdots, N\}$, we find

$$\mathcal{W}_{\mathrm{E}\to\mathrm{S}} = \sum_{j\in\mathrm{E}}\sum_{i\in\mathrm{S}} \mathcal{W}_{j\to i} = \Delta\left(\sum_{i=1}^{M} \mathcal{K}_i + \sum_{k>i=1}^{M} \mathcal{V}_{ik}\right) \equiv \Delta\mathcal{E}_{\mathrm{S}}. \tag{2.5}$$

Therefore, in this fundamental, microscopic, mechanical, conservative framework, no ambiguity arises concerning the notion of internal energy, and there is no need for one to conceive either uncontrollable or inaccessible forms of energy transfer, such as heat. Indeed, the notion of heat appears only artificially in mechanics, in cases when the microscopic degrees of freedom cannot be tracked, often due to a large number of particles. For example, when a block slides with friction on a table, the table is expected to heat up, due to the friction with the block. This transference of energy to the microscopic degrees of freedom of the table and block can be considered as heat. However, if we could access and describe all the degrees of freedom of the particles that make up the table and block (so as to account

$\mathcal{W}_{\mathrm{E}\to\mathrm{S}}$ and $\Delta\mathcal{E}_{\mathrm{S}}$ for their particles), we would verify that only mechanical work was done on the particles[1].

Eq. (2.5) can be deduced for many systems, but it is usually taken as the following principle of mechanics [91]:

Principle 1. ***(Work-Energy)*** *Work done on a given system of interest* S *will equal the change in its internal energy.*

Therefore, if one can unambiguously identify the internal energy of a given system S (for instance by "turning off" all interactions with the environment), then one can take the Work-Energy principle as a fundamental postulate, from which the work done on S by E is computed as $\Delta\mathcal{E}_{\mathrm{S}}$. Conversely, if the interactions with S are known and one is able to compute the total work done on it, then it will equal the variation of the internal energy of S. Consequently, a mechanical definition of work has two important features: not only can we describe how each particular system does work on another but also properly characterize internal energy and its remarkable relation with work, as portrayed in the Work-Energy principle.

2.1.1 Distributions in classical mechanics

The mechanical approach presented so far can be naturally extended so as to encompass classical distributions, using the Liouvillian formalism. Take, for instance, the N particles interacting in Eq. (2.2). We can assign an initial classical distribution $\varrho(\Gamma_0)$ to the points $\Gamma_0 = (x_1^0, x_2^0, ...x_N^0, p_1^0, p_2^0, ...)$ of phase space. From the methods of classical mechanics, it is, in principle, possible to obtain the solution $\Gamma_t \equiv \Gamma_t(\Gamma_0, t)$ corresponding to the evolved phase space point at any time t, which is initially located at Γ_0; in particular, this allows us to compute the position $x_2^t \equiv x_2^t(\Gamma_0, t)$ and momentum $p_2^t \equiv p_2^t(\Gamma_0, t)$ of particle 2 for any time t. Also, we can speak of the resultant force made on 2 at instant t, given the initial condition Γ_0: $f_{\mathrm{res}}^t \equiv f_{\mathrm{res}}^t(\Gamma_0, t) = \frac{d}{dt}p_2^t$. It follows that the resultant mechanical work done on particle 2, during the interval $[t_1, t_2]$ for any initial configuration Γ_0, is computed as:

$$\mathcal{W}_{\mathrm{E}\to\mathrm{S}}(\Gamma_0, t_2, t_1) = \int_{t_1}^{t_2} \frac{f_{\mathrm{res}}^t\, p_2^t}{m_2}\, dt = \frac{1}{2m_2}\left[(p_2^{t_2})^2 - (p_2^{t_1})^2\right]. \tag{2.6}$$

In other words, resultant mechanical work can be seen as a function of points of the initial phase space configuration Γ_0, t_1, and t_2. This element has no intrinsic fluctuation on its own; it is a well-defined element of the classical reality[2]. However, when we are ignorant about

[1] When a macroscopic body is said to be heated, the molecules that compose it receive energy from external bodies. This energy is transferred through physical interactions that are fundamentally conservative, independent of velocity, so as to be computed as mechanical work associated with the corresponding conservative forces between them. Therefore, in a microscopic scale, all the internal energies are transferred by means of mechanical work. An insightful approach to conservative potentials and their role in mechanics is given in the reference [90].

[2] For a more detailed discussions on elements of reality, we refer the reader to the discussions in Section 2.8.

the precise initial conditions, then we cannot predict work in a single run of the dynamics. Its value can certainly vary from one run to another, so that we can think of (ignorance-based) fluctuations. In this scenario, our predictions are limited to probability distributions and the n-th statistical moment of work,

$$\langle \mathcal{W}^n_{\mathrm{E}\to\mathrm{S}}(t_2,t_1)\rangle_{\varrho} = \int \mathrm{d}\Gamma_0 \; \mathcal{W}^n_{\mathrm{E}\to\mathrm{S}}(\Gamma_0,t_2,t_1)\,\varrho(\Gamma_0), \tag{2.7}$$

where $\mathrm{d}\Gamma^0 = dx^0_1 dx^0_2 \cdots$ is the differential volume around the phase space point Γ_0. Moreover, we can obtain expressions for $\langle g(\mathcal{W}_{\mathrm{E}\to\mathrm{S}}(t_2,t_1))\rangle_{\varrho}$ for any distribution $\varrho(\Gamma_0)$ and sufficiently smooth function g, by the replacement $\mathcal{W}^n_{\mathrm{E}\to\mathrm{S}} \to g(\mathcal{W}_{\mathrm{E}\to\mathrm{S}})$ in (2.7).

Because of the initial ignorance, the resultant force and velocity can vary from a run to another, meaning that they can be ascribed statistical fluctuations. Over the ensemble, we can predict $\langle f^t_{\mathrm{res}}\rangle$ and $\langle v_2(t)\rangle$, with their respective variances and n-th statistical moments; in the same way, the definition of mechanical work $\mathcal{W}_{\mathrm{E}\to\mathrm{S}}(\Gamma_0,t_2,t_1)$ and its statistical moments computed from (2.7) are preserved. Moreover, we emphasize that the distribution $\varrho(\Gamma_0)$ can be of any kind: it can be either a gaussian distribution or related with a thermal bath; it may have correlations or express a subjective or objective ignorance (stochasticity) with respect to the system.

Naturally, we are not limited to a single-particle system; indeed, had we considered an interest system S with M particles, then we would as well arrive at an expression like (2.5) for any initial point Γ_0. In this sense, the discussion on internal energy and Work-Energy principle can as well be posed here. Moreover, we also can deduce the following expression for the n-th statistical moment of $\mathcal{W}_{\mathrm{E}\to\mathrm{S}}$:

$$\begin{aligned} \langle \mathcal{W}^n_{\mathrm{E}\to\mathrm{S}}(t_2,t_1)\rangle_{\varrho} &= \langle (\mathcal{E}_{\mathrm{S}}(t_2)-\mathcal{E}_{\mathrm{S}}(t_1))^n\rangle_{\varrho} \\ &= \int \mathrm{d}\Gamma_0 \; (\mathcal{E}_{\mathrm{S}}(\Gamma_0,t_2)-\mathcal{E}_{\mathrm{S}}(\Gamma_0,t_1))^n\,\varrho(\Gamma_0), \end{aligned} \tag{2.8}$$

where $\mathcal{E}_{\mathrm{S}}(\Gamma_0,t_2)-\mathcal{E}_{\mathrm{S}}(\Gamma_0,t_1)$ is the change in the internal energies in the interval $[t_1,t_2]$ for a given initial configuration Γ_0. Eq. (2.8) can thus be seen as a weak form of the Work-Energy principle.

In order to link our discussion to Sections 2.7 and 2.8, we should remark that one can compute $\langle (\mathcal{E}_{\mathrm{S}}(t_2)-\mathcal{E}_{\mathrm{S}}(t_1))^n\rangle_{\varrho}$ as well as $\langle g(\mathcal{E}_{\mathrm{S}}(t_2)-\mathcal{E}_{\mathrm{S}}(t_1))\rangle_{\varrho}$ in an alternative way. We can define a distribution $\wp_{\mathrm{S}}(\Delta,t_2,t_1)$ corresponding to the probability density function of S of varying its energy by an amount Δ during the interval $[t_1,t_2]$. By defining the conditional distribution $\wp(\Delta|e_2,e_1) = \delta(\Delta-(e_2-e_1))$ of the amount of change in the energy Δ of being equal to the difference between the energies e_2 and e_1 at instants t_1 and t_2 respectively, then $\wp_{\mathrm{S}}(\Delta,t_2,t_1)$ can be expressed as

$$\wp_{\mathrm{S}}(\Delta,t_2,t_1) = \iint_{e_2,e_1} d_{e_2}\, d_{e_1}\, [\wp(\Delta|e_2,e_1)\wp_{e_2,e_1}] \tag{2.9}$$

where $\wp_{e_2,e_1}$ is the joint probability density function

$$\wp_{e_2,e_1} = \int_{\Gamma_0} d\Gamma_0 \wp(e_2,e_1|\Gamma_0)\varrho(\Gamma_0). \tag{2.10}$$

corresponding to the event of obtaining value e_1 at time t_1 and e_2 at time t_2, given the initial distribution $\varrho(\Gamma_0)$. Notably, in Eq. (2.10), the conditional distribution can be expressed as $\wp(e_2, e_1|\Gamma_0) = \delta(\mathcal{E}_{\mathrm{S}}(\Gamma_0, t_1) - e_1)\delta(\mathcal{E}_{\mathrm{S}}(\Gamma_0, t_2) - e_2)$. Having an explicit expression for $\wp_{\mathrm{S}}(\Delta, t_2, t_1)$, the computation of $\langle g(\mathcal{E}_{\mathrm{S}}(t_2) - \mathcal{E}_{\mathrm{S}}(t_1))\rangle_{\varrho}$ is direct:

$$\langle g(\mathcal{E}_{\mathrm{S}}(t_2) - \mathcal{E}_{\mathrm{S}}(t_1))\rangle_{\varrho} = \int d\Delta\, \wp_{\mathrm{S}}(\Delta, t_2, t_1) g(\Delta). \tag{2.11}$$

It is not hard to show that computing averages with (2.8) or using the distribution $\wp_{\mathrm{S}}(\Delta, t_2, t_1)$ leads to the same results.

2.2 Thermodynamics work: from equilibrium thermodynamics to stochastic thermodynamics

Although subtle, there is an important distinction between the description of work coming from mechanics and thermodynamics. To appreciate this point, consider a very simple model depicted in Fig. 2.1. It is an ideal gas of M monatomic particles that roughly do not interact with each other, all of them confined in a container. The gas and container are initially in equilibrium with a cold reservoir (Fig. 2.1(a)), so that we can assign a temperature T_{c} to the gas, and its average internal energy can be described, from statistical physics [40], as $\langle \mathcal{E}_{\mathrm{S}}(t_1)\rangle = \langle \sum_{i=1}^{M} \mathcal{K}_i\rangle = \frac{3}{2} M k_{\mathrm{B}} T_{\mathrm{c}}$, where $\mathcal{K}_i$ refers to the kinetic energy of particle i and k_{B} is the Boltzmann constant. Now, suppose that we take the gas+container system out of the cold reservoir and put it in contact with another hot reservoir (Fig. 2.1(b)), so that, the gas+container and the hot reservoir exchange energy (Fig. 2.1(c)) and the system + container + reservoir reach equilibrium (Fig. 2.1(d)). At this moment, a temperature T_{h} can be assigned to the gas. After the equilibrium is attained, the internal energy of the gas is $\langle \mathcal{E}_{\mathrm{S}}(t_2)\rangle = \langle \sum_{i=1}^{M} \mathcal{K}_i\rangle = \frac{3}{2} M k_{\mathrm{B}} T_{\mathrm{h}}$. As a result of the process, an amount $\langle \mathcal{E}_{\mathrm{S}}(t_2)\rangle - \langle \mathcal{E}_{\mathrm{S}}(t_1)\rangle = \frac{3}{2} M k_{\mathrm{B}}(T_{\mathrm{h}} - T_{\mathrm{c}})$ is transferred to the gas. We may then ask ourselves: which kind of energy was transferred in this simple scenario? The explanation may be quite different depending whether we departure from a thermodynamical or a mechanical perspective.

Under thermodynamical lenses, the usual explanation [2] is that all the variation of internal energy $\langle \mathcal{E}_{\mathrm{S}}(t_2)\rangle - \langle \mathcal{E}_{\mathrm{S}}(t_1)\rangle$ is considered to be heat supplied by the hot reservoir and no thermodynamics work is done on the gas. Indeed, we cannot perceive macroscopic changes in the boundaries of the systems. On the other hand, in a microscopic mechanical perspective, work must be done in the gas particles: roughly, by a straightforwardly application of the Work-Energy principle or Eq. (2.8), we have that $\langle \mathcal{E}_{\mathrm{S}}(t_2)\rangle - \langle \mathcal{E}_{\mathrm{S}}(t_1)\rangle = \langle \mathcal{W}_{\mathrm{E}\to\mathrm{S}}\rangle$. Since the particles of the gas are supposed to not strongly interact with each other, then the changes in their kinetic energies must averagely come from external work done on them by the particles of the container. Therefore, if we depart from a thermodynamics basis, all we see is heat, without any form of energy transfer that we would call work. On the other hand,

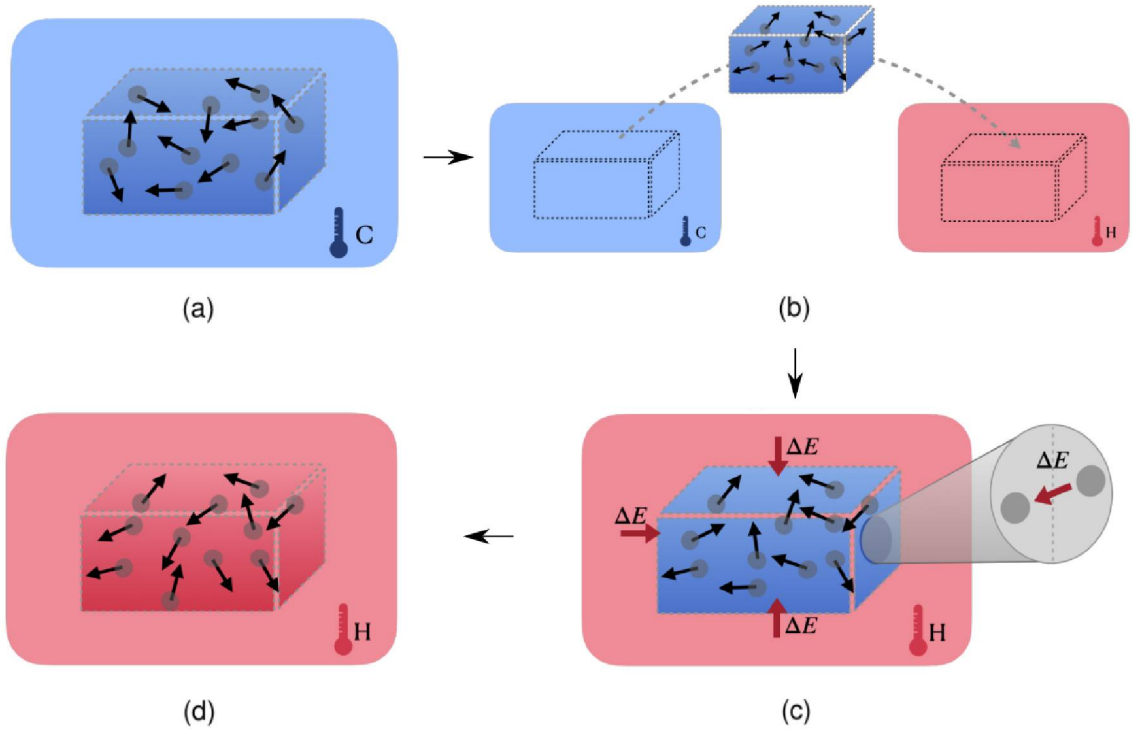


Figure 2.1 – M particles confined by a container, exchanging energy with reservoirs. The gas+container system is submitted to the following process: (a) the gas+container system is initially in thermal equilibrium with the cold reservoir at temperature T_{c}; (b) the gas+container is removed from the cold reservoir and put in contact with the hot reservoir at temperature T_{h}, so that (c) the gas particles and the surroundings begin to exchange energy and (d) after a sufficiently great time t_2, the gas+container system is in equilibrium with the hot reservoir. During the whole process, the description of work is quite different when considering the concept defined in mechanics from that of thermodynamics. In a macroscopic thermodynamics sense, only heat is transferred to the gas and no work is done. On the other hand, in a mechanical microscopic perspective point of view (Fig. 2.1(c)), all the energy transferred is accounted as mechanical work done by the particles of the walls on the particles of the gas. This differences highlights how distinguished the formulations of work coming from each theory are.

in mechanics, due to the Work-Energy principle, the energy variation must be accounted as work resulting from the interactions between the gas particles and the walls.

This is not to say that we have a contradiction between both scenarios: it is just that the concept of work coming from each theory is grounded on different basis. Such a difference is not important in many usual situations, as the conditions and configurations of thermodynamics systems are frequently different from those of mechanics. However, as we aim at a description of work for general microscopic scenarios and extend it to the quantum framework, these nuances must be clarified. With this view in mind, we investigated the literature, searching for thermodynamics definitions of work so as to compare them with the mechanical description. The rest of this section is devoted to present the outcome of our research.

2.2.1 Equilibrium thermodynamics and statistical physics definitions

Many ways of defining work were enunciated in the context of equilibrium thermodynamics. Some authors [13, 14] assume that it is grounded on other theories' definitions. For instance, the form $-p_{\text{isos}}dV$ comes from the kinetic theory of gases, where p_{isos} is the isostatic pressure of a gas and V its confinement volume; also, BdM comes from electrodynamics theory, with B denoting an external magnetic field applied to a system with magnetization M. In this context, microscopic work done between particles is not taken into account and thermodynamic work is related to macroscopic properties.

Other authors [15] proposed that thermodynamic work is the external work that a system of interest does on an environment, so that some kind of displacement occurs: "the raising or lowering of a suspended weight, the winding or unwinding of a spring, or, in general, the alteration of the position or configuration of some external mechanical device". On the other hand, work can be defined indirectly through heat [92]: heat is seen as the form of energy transferred spontaneously to a system, so that work would be any other form of energy transfer in order for the first law of thermodynamics to be satisfied.

Some different perspectives of work were addressed in the scope of equilibrium thermodynamics in an engineering-oriented approach. It was argued that heat is the form of energy transferred between two systems due to a temperature difference, so that there can be no heat transfer between two systems of the same temperature [1]; if energy is transferred to a system and that transfer is not characterized as heat, then it must be work. On the other hand, in the reference [2] it was argued that thermodynamic work is done by a system on its surroundings if the only net effect on everything outside the system could have been the lifting of a weight. In other words, if the external environment could be replaced by a weight being lifted and nothing changed in the system of interest, then thermodynamic work can be said to be done on the environment by the system of interest. Heat then accounts for energy transfers that cannot be work.

Although the perspectives of work are not the same in these various approaches, we can say that they converge by assimilating thermodynamics work with a form of energy transfer associated with macroscopicity, control and utility. On one hand, when thermodynamic work is defined from known forms coming from other theories, work is computed regarding macroscopic properties of the system such as volume, magnetization, polarization, among others [1]. On the other hand, when work is defined as the transfer of energy other than heat, then heat, being a form of energy transfer associated with microscopic energetic changes, causes all other forms of energy transferred in a macroscopic manner to be defined as work.

Statistical physics was born due to the demand of explaining thermodynamic results from a mechanical substrate. As a result, more precise forms of defining work were pursued, accurately characterizing how the macroscopicity and usefulness of the thermodynamic definition can be understood in a statistical physics context. A form of work proposed in the context of statistical physics that could later be adapted to quantum thermodynamics

was built based on what we will call here Non-Fluctuating Variable (NFV), for reasons to be discussed next[3] [16–18, 39, 40, 93]. Examples are the volume of a gas, the magnetization of a material, the deformation of an elastic band, among others. These variables account for what may be called the macroscopic displacement or variable of the system. Denoting them by λ, the energy transferred from a change in these variables is what we call statistical physics work $\mathcal{W}_{\rm sp}$, so that

$$\delta\mathcal{W}_{\rm sp} = (\partial_\lambda E_{\rm S})\, d\lambda \equiv f_\lambda d\lambda, \tag{2.12}$$

where $\partial_\lambda E_{\rm S} = f_\lambda$ is the generalized force [93]. Following the usual prescription of statistical physics, we take the internal energy as the average value of the Hamiltonian function (or operator), so that $E_{\rm S} = \langle\mathcal{H}\rangle_\varrho = \int_\Gamma \varrho\mathcal{H}(\Gamma)d\Gamma$. $\mathcal{W}_{\rm sp}$ can then be computed as [17, 40]

$$\delta\mathcal{W}_{\rm sp} = \partial_\lambda\langle\mathcal{H}(\lambda)\rangle\, d\lambda. \tag{2.13}$$

Eq. (2.12) establishes a criterion differentiating reservoirs of work (batteries) and heat, often used in the quantum context [5, 52–54]: a battery or work reservoir must be such that the energy supplied or received is in the form (2.12). As we will see in Section 2.4, this criterion is not always taken into account in the literature and, as smaller systems are considered, the distinction between work and heat reservoirs may not be sufficiently clear.

Commonly in the context of statistical physics and stochastic thermodynamics, an explicit time dependence is given for λ and this is called an external variable/parameter, since its dynamics are not described by $\mathcal{H}(\lambda)$ [19]. For example, we can compute the work done on a piston by a gas when controlling the position of the piston's center of mass L, so that $L = \lambda = \lambda(t)$. In the Fig. (2.2), we show some statistical microstates of an ensemble in which this explicit temporal dependence is imposed on L.

Once a temporal function is assigned to $L_t = \lambda(t)$, we can construct an effective Hamiltonian $\mathcal{H}_{\rm eff}(\lambda(t))$ for the dynamics of the gas so the definition (2.13) can be used. Considering that $\lambda(t)$ does not change rapidly so that the process occurs in quasi-equilibrium, then one can deduce[4] that the statistical physics work done by the gas on the piston can be written as $\delta\mathcal{W}_{\rm sp} = \partial_\lambda\langle\mathcal{H}_{\rm eff}(\lambda(t))\rangle d\lambda = \partial_\lambda\langle\mathcal{H}_{\rm eff}(\lambda(t))\rangle\dot{\lambda}\, dt = -p_{\rm isos}dV$. That is, it is possible to deduce a form commonly used in thermodynamics, from the definition $\delta\mathcal{W}_{\rm sp}$, with an explicitly time-dependent function $L = \lambda(t)$.

However, one might question whether λ must necessarily be explicitly time-dependent. In fact, perhaps one of the most explicit ways of defining NFVs was established in [17], by the statement[5]:

"In the corresponding statistical treatment we can assign to all the systems in the representative ensemble the same value of the external coordinates as those of the thermo-

[3] In Ref. [17], these variables are called external. In order to avoid some theoretical confusion with this naming, we use NFV to distinguish them from external ones.

[4] See Section 2.4 of [40].

[5] Taken from page 527 of [17].

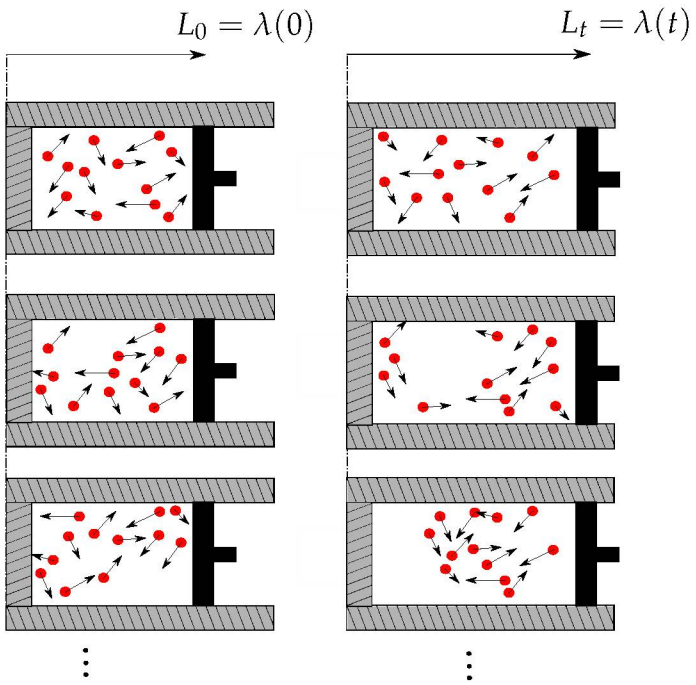


Figure 2.2 – Some microstates of the piston+gas system, in which a time function is imposed on the position of the piston's center of mass: at instant 0, the piston is located at position $L_0 = \lambda(0)$ with respect to the left end of the box. The piston is then moved to $L_t = \lambda(t)$, in a quasi-equilibrium process. Using the expression (2.13), it is possible to deduce that $\delta\mathcal{W}_{\text{FE}} = -p_{\text{isos}}dV$, where V is the volume occupied by the gas and $-p_{\text{isos}}$ is the isostatic pressure of the gas.

dynamic system of interest, and can represent the corresponding generalized forces by their average values in that ensemble".

In other words, the NFVs λ (denoted by Tolman as external) are taken to be fixed throughout the ensemble, i.e. given a certain statistical ensemble describing a macroscopic system, these variables will have the same value for each element of the ensemble (microstate) in a certain time interval analyzed. Therefore the variables λ can be defined as those *that do not fluctuate significantly over a time interval*. Formally, we define the following criterion, referred to us as Tolman's criterion:

Criterion 1. ***(Tolman)*** *The variables of a given system of interest are Non-Fluctuating Variables (NFVs), if they have negligible fluctuations, that is, if for a given distribution describing the system of interest, the values of these variables are practically the same in all microstates of the system.*

We note, therefore, that the denomination of Non-Fluctuating Variables NFVs is indeed consistent. To properly understand the perspective of Tolman's criterion and the reason for considering external variables as special cases of NFVs, we can look again at the case of the piston+gas system, now represented in Fig. 2.3, where the piston expands almost statically due to the addition of heat by a flame.

The volume of the gas (or the position of the piston) is fixed for all elements that make up the ensemble at the interval of time $[0, t]$, even though an explicitly time-dependent function

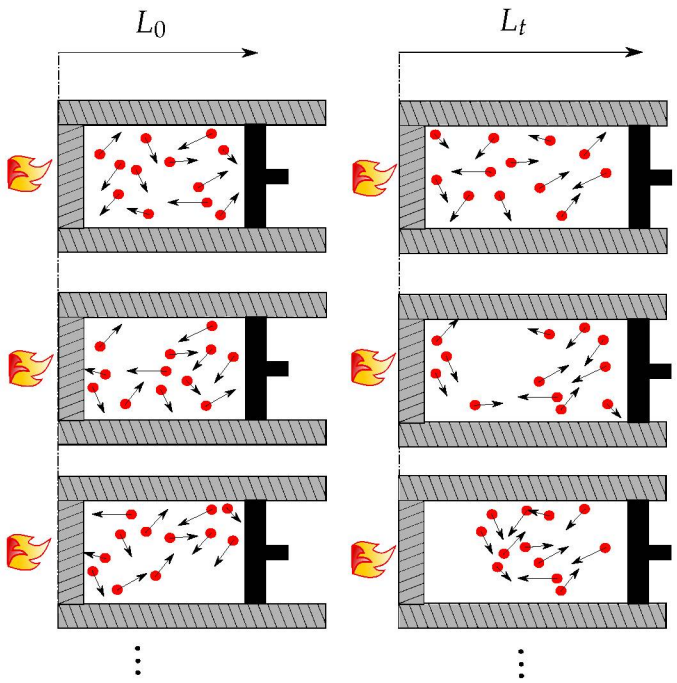


Figure 2.3 – Some microstates of the piston+gas system, heated by a flame at two instants: at instant 0, a flame is placed on the left side of the box, located at L_0, the piston moves and the gas expands until t, the piston reaches the position L_t. In both cases, the positions L_0 and L_t of the piston are approximately the same for each microstate of the system, satisfying Tolman's criterion. Note that no *explicit* time dependency is assumed for L, since the flame on the left makes the piston expand.

was not imposed to it. Although the gas particles vary in position or momentum in each microstate, and these same particles can induce the piston to move, the position of the piston and its motion will be approximately the same for all microstates of the ensemble representative of the macroscopic piston+gas system. If we assume that this behavior will be maintained for a certain time interval then the volume (or the piston position) can be taken as NFV. Also, as shown in Section 7.4, we note that it is possible again to obtain the usual expression $\delta\mathcal{W}_{\text{sp}} = -p_{\text{isos}}dV$, considering the fluctuations of the position and velocity of the piston's center of mass negligible.

The notion of thermodynamic work as something useful and macroscopic, also explored in the scope of statistical physics, is consistently encapsulated in the definition of NFVs and in Tolman's criterion: being of low fluctuation (relatively small mean square deviation), NFVs do not vary appreciably from one round of the experiment to another, which guarantees significant predictability about their values. In particular, when an explicit temporal dependence is specified and imposed to a given system variable, this variable will still be described as a NFV whose dynamics are described *a priori*. However, because their dynamics are imposed, these NFVs are called as external variables in this particular case.

2.2.2 Classical stochastic thermodynamics and its Fluctuation Theorems

Thermodynamics has been extended so as to be applied to smaller mesoscopic systems, where assumptions such as equilibrium, weak coupling, or large numbers of particles are relaxed, and fluctuations have a key role. In this context, stochastic thermodynamics emerged in order to analyze systems outside the usual equilibrium thermodynamics scope [19, 20]. The natural step to define work was to extend the statistical physics notion so as to fit such a scenario. However, great care is needed when defining NFVs. The path traced in the literature was to consider them as external variables, i.e. explicitly time-dependent functions $\lambda \equiv \lambda(t)$. Consequently, the time-dependent hamiltonian $\mathcal{H}(\lambda(t)) \equiv \mathcal{H}(t)$ is induced by the NFV $\lambda(t)$. Therefore, in the context of stochastic thermodynamics, a work formulation is naturally induced from the physical-statistical definition (2.13), which we will refer to as the Hamiltonian-Based (HB) definition: work $\mathcal{W}_{\mathrm{hb}}$ done on a system described by a Hamiltonian function $\mathcal{H}(\lambda(t))$ is computed as

$$\delta\mathcal{W}_{\mathrm{hb}} \coloneqq (\partial_\lambda \mathcal{H})\,\dot{\lambda}\,dt \equiv \partial_t \mathcal{H}\,dt. \tag{2.14}$$

A very intuitive example, depicted in Fig. 2.4, of a system using such a definition was used by Jarzynski in his review article [94], in which the Hamiltonian is described as

$$\mathcal{H} = \sum_{i=1}^{3} \frac{p_i^2}{2m_i} + \sum_{k=0}^{3} \mathcal{V}\left(x_{k+1} - x_k\right), \tag{2.15}$$

where x_i, p_i represent the position and momentum of each particle i, with the position of particle 4 being $x_4 = \lambda(t)$, and the particle 0 is represented by a wall located at $x_0 = 0$. $\Gamma = \{x_1, x_2, \cdots p_2, p_3\}$ denotes the phase space point of the 3 remaining particles system.

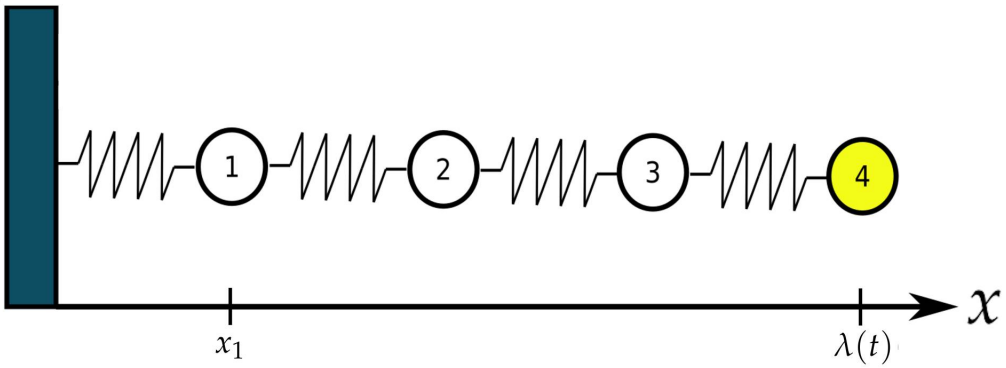


Figure 2.4 – Four particles attached to a wall by means of particle 1. The position of particle 4, $x_4 = \lambda = \lambda(t)$, and of the wall, $x_0 = 0$, are imposed at all times, with prescribed protocols for their positions. If a distribution is attributed to particles 1, 2 and 3, various configurations of their positions are possible, although λ remains fixed for the entire ensemble.

If a distribution $\varrho(\Gamma_0)$ is initially defined in phase space, some possibilities for the positions of particles 1, 2 and 3 can be described. Note that the position x_4 as well as x_0 will be the

same in all ensemble representations of the system, since their dynamics are defined a priori by $\lambda(t)$ and 0, respectively. In this sense, from the expression (2.14) and considering the initial distribution for the four-particle system as a whole, the HB work expression is

$$\langle \mathcal{W}_{\mathrm{hb}}(t,0)\rangle = \int_0^t \langle \partial_\lambda \mathcal{H}\rangle\, \dot{\lambda}\, dt' = \int_0^t \partial_\lambda \left(\int_{\Gamma_0} \varrho(\Gamma_0)\mathcal{H}(\Gamma_{t'}(\Gamma_0,t'),\lambda(t'))d\Gamma_0 \right) \dot{\lambda}\, dt'. \quad (2.16)$$

Heat, on the other hand, is connected with the variation of the distribution $\varrho_t(\Gamma_t)$: since the thermodynamic average internal energy is defined as $\langle \mathcal{H}\rangle$, then from the first law of thermodynamics it is natural to define

$$\delta\mathcal{Q}_{\mathrm{hb}} \coloneqq \int_\Gamma (\partial_t \varrho(t))\mathcal{H}(\Gamma_t,\lambda(t))d\Gamma dt = \frac{d}{dt}\langle \mathcal{H}(t)\rangle dt - \delta\mathcal{W}_{\mathrm{hb}} \quad (2.17)$$

as the heat transferred to the system of interest. It is possible to show that an analogue to the second law of thermodynamics can be obtained from this definition of heat when states close to equilibrium are considered [40]. For more general situations, alternative forms of the second law accounting correlations can be obtained [20, 95, 96].

The definitions (2.14) and (2.17) can be extended, in order to also account the presence of a thermal bath and strong interactions between the environment and the system of interest. In this context, the Hamiltonian can be described as [88]

$$\mathcal{H}(t) = \mathcal{H}'\left(\Gamma_{\mathrm{S}},\lambda\right) + \mathcal{V}_{\mathrm{int}}(\Gamma_{\mathrm{S}},\Gamma_{\mathrm{E}}) + \mathcal{H}_{\mathrm{E}}\left(\Gamma_{\mathrm{E}}\right), \quad (2.18)$$

with Γ_{S} and Γ_{E} denoting points in phase space referring respectively to the system of interest and the environment. $\mathcal{H}' = \mathcal{H}'(\Gamma_{\mathrm{S}},\lambda(t))$[6] accounts for the inclusive internal energy (see the next section) of the system of interest S, described as a function of a time-dependent NFV $\lambda(t)$, $\mathcal{V}_{\mathrm{int}}(\Gamma_{\mathrm{S}},\Gamma_{\mathrm{E}})$ describes the interaction between S and the environment, and $\mathcal{H}_{\mathrm{E}}\left(\Gamma_{\mathrm{E}}\right)$ corresponds to the energy of the environment. Computing the HB work for this system, we have $\mathcal{W}_{\mathrm{hb}}(t,0) = \int_0^t dt' \dot{\lambda}\partial_\lambda \mathcal{H}'$, which was interpreted both as thermodynamic work done on the system of interest S and thermodynamic work done on the system as a whole in Ref. [88]. Taking $\mathcal{H}'$ as internal energy and considering the first law of thermodynamics, we have that heat, defined by $\mathcal{Q} = \Delta\mathcal{H}' - \mathcal{W}_{\mathrm{hb}}$, can be written as

$$\mathcal{Q} = \int_0^t dt' \dot{x}\, \partial_x \mathcal{H}'. \quad (2.19)$$

Work as in Eq. (2.16) can also be computed for general systems as follows: let the "accumulated" work $w(\Gamma_0,t,0)$ be defined as the energy change $\mathcal{H}(\Gamma_t,t) - \mathcal{H}(\Gamma_0,0) \equiv \mathcal{H}(\Gamma_t(\Gamma_0,t),\lambda(t)) - \mathcal{H}(\Gamma_0,0)$ for an element of the phase space that is at the point Γ_0 initially and reaches $\Gamma_t = \Gamma_t(\Gamma_0,t)$ after an interval t; the average of all possible trajectories and therefore of all possible accumulated work w computed in this way is just $\langle \mathcal{W}_{\mathrm{hb}}(t,0)\rangle$. Taking this view of work for general classical systems and initially considering a Boltzmann-Gibbs distribution $\varrho(\Gamma_0) = (1/\mathcal{Z}_0)\mathrm{e}^{-\beta\mathcal{H}(\Gamma_0,\lambda_0)}$ with inverse temperature $\beta = (k_B T)^{-1}$ and

[6] As discussed in Section 2.3, this portion of energy accounts for the interaction of the system of interest with the agent that performs work by means of λ.

partition function as $\mathcal{Z}_t = \int_{\Gamma_t} \exp[-\beta\mathcal{H}(\Gamma_t, t)]d\Gamma_t$, Jarzynski deduced the bold equality that bears his name [22]:

$$\langle \exp(-\beta\mathcal{W}_{\mathrm{hb}}(t,0))\rangle = \mathcal{Z}_t/\mathcal{Z}_0. \tag{2.20}$$

This relation has been tested experimentally for classical systems [21, 36] and provides an interesting basis for practical purposes: one is usually interested in the thermodynamic direction of a process (if the process is spontaneous or not) or other informations that can be obtained from the Helmholtz free energy $F(t) = -k_{\mathrm{B}}T\ln(\mathcal{Z}_t)$; however, the theoretical description of $\mathcal{Z}_t$ is often difficult to obtain and experimentally undetermined for complex mesoscopic systems [47]. So, instead of waiting for a system to reach equilibrium to obtain expressions for $F(t) - F(0) = -\ln(\mathcal{Z}_t/\mathcal{Z}_0)$, one can compute work for a sufficiently high number of copies of the system, in a finite interval of time, so as to compute $\langle \exp(-\beta\mathcal{W}_{\mathrm{hb}})\rangle$, and determine, from Jarzynski equality, the ratio $\mathcal{Z}_t/\mathcal{Z}_0$ and, therefore, $F(t) - F(0)$.

Jarzynski's seminal relation and its extensions [88, 89] to more general systems like (2.18) can be seen as special cases of a more general class of the so-called Fluctuation Theorems (FTs). In general, FTs are exact equalities that make use of microscopic symmetries to derive constraints on thermodynamics properties, which have broad their extensions to ever more general scenarios, being deduced in the context of stochastic thermodynamics and quantum thermodynamics [21, 65, 67, 68]. Though work FTs are arguably the most studied, FTs constraining other thermodynamics quantities, such as entropy production [71], have also been derived in the literature[7].

Recently, it has been noticed that FTs analogous to Jarzynski [45] based, however, on another formulation of work, have been deduced still in the seventies [23]. Considering that two possible formulations could then be proposed for work (Eqs. (2.1) and (2.14)), a discussion through a series of articles [47–50] occurred, placing under scrutiny the definition of internal energy and work; a discussion which we consider next.

2.3 Internal energy?

From the previous discussions, it is notable that the concept of internal energy is strongly connected to the concept of work, both in classical mechanics and thermodynamics. A possible question to ask is whether both theories agree on the definition of internal energy. Additionally, one might question whether both the mechanical and thermodynamic definitions of work yield the same results for small-sized systems, as those being analyzed in the scope of stochastic thermodynamics.

Let us take the following Hamiltonian function, usually considered in the context of stochastic thermodynamics [45–50]:

$$\mathcal{H}(t) = \mathcal{H}_0(x) - \lambda(t)x + g(t), \tag{2.21}$$

[7] See the references in [20, 21] for more details.

where x denotes the coordinate of a system of interest S whose undisturbed dynamics is described by the so-called bare Hamiltonian function $\mathcal{H}_0(x)$ [45] and $\lambda(t)$ is the driving force protocol on S.

On the one hand, mechanical work is unambiguously described by (2.1), *viz.* $\mathcal{W} = \int_C f dx$. Therefore, if we consider a (Heaviside) step function $\Theta(t)$ for the force protocol, such that $f = \lambda(t) = f_0\,\Theta(t)$ in (2.21), then work done by the force $\lambda(t)$ will be

$$\mathcal{W}_{\mathrm{E}\to\mathrm{S}}(t,0) = \int_0^t \lambda \frac{dx}{dt} dt = f_0 \int_0^t dx = f_0(x(t) - x(0)). \tag{2.22}$$

Moreover, using this mechanical view of work, the fundamental equality

$$\langle \exp(-\beta \mathcal{W}_{\mathrm{E}\to\mathrm{S}}) \rangle = 1, \tag{2.23}$$

was deduced considering, in the same way as in Eq. (2.20), an initial Boltzmann-Gibbs distribution with inverse temperature β. This equality was first deduced by Bochkov and Kuzovlev in 1977 [23] (which we will label as BK equality).

In the usual context of stochastic thermodynamics, on the other hand, the HB work formulation (Eq. (2.14)) can be used:

$$\mathcal{W}_{\mathrm{hb}} \equiv \int_0^t (\partial_{t'} \mathcal{H}(\lambda(t')))dt' = \int_0^t \frac{d\mathcal{H}(\lambda(t'))}{dt'} dt' = \mathcal{H}(\lambda(t)) - \mathcal{H}(\lambda(0)) = \Delta\mathcal{H}, \tag{2.24}$$

for any force protocol λ. Moreover, as we saw before, Jarzynski relation (2.20) holds for the HB definition.

As a result, two different results were obtained when computing work from classical mechanics (Eq. (2.22)) and stochastic thermodynamics (Eq. (2.24)) when $\lambda(t) = f_0\Theta(t)$. Moreover, different FTs were obtained, *viz.* BK (Eq. (2.23)) and Jarzynski (Eq. (2.20)) equalities. Taking into account these significant differences, a series of discussions took place in the literature.

Vilar and Rubi [47] noticed, by inspection of Eq. (2.24), that an arbitrary term $g(t) - g(0)$ would appear as part of the free energy computed via HB, which in principle has no apparent physical meaning. For the authors, their results show that the HB definition cannot be applied straightforwardly to *all* systems with explicit temporal dependence. Peliti [32,51], on the other hand, stated that the function $g(t)$ that enters the Hamiltonian (2.21) does not refer to an arbitrary term and in fact depends on the interaction between the system of interest and the external systems acting on it. In this sense, he treated some examples related to electric and gravitational fields in which $g(t)$ is explicitly non-arbitrary.

Despite this dispute surrounding two perspectives of work, it was later accepted by the community [21,45,46] that different works were being computed in (2.22) and (2.24). Fixing $g(t) = 0$ in Eq. (2.21), the classical mechanics work gives us

$$\mathcal{W}_{\mathrm{E}\to\mathrm{S}}(0,t) = \int_0^t f \frac{dx}{dt} dt = \int_0^t \lambda \frac{dx}{dt} dt = \Delta\mathcal{H}_0, \tag{2.25}$$

since $\frac{d\mathcal{H}_0}{dt} = \frac{d(\mathcal{H}(t)+\lambda(t)x)}{dt} = \frac{\partial\mathcal{H}(t)}{\partial t} + \frac{d(\lambda(t)x)}{dt} = \lambda(t)\dot{x}$. In this context, the Work-Energy principle from mechanics (Principle 1) can be stated in this effective, stochastic thermodynamics scenario. On the other hand, as argued by Horowitz, Jarzinsky, and Peliti [32, 45, 46, 50, 51], the Work-Energy principle of classical mechanics would still be preserved for the HB definition, with, however, *the interaction term being counted as part of the internal energy*[8], that is, $\mathcal{W}_{\mathrm{hb}} = \Delta E_{\mathrm{S}}$, provided that $E_{\mathrm{S}} = \mathcal{H}(t) = \mathcal{H}_0(x) - \lambda(t)x$. Therefore, it was convenient to denote the definitions HB as the *inclusive* formulation of work, emphasizing the inclusion of the interaction as part of the internal energy of the system; the approach of Eq. (2.25), which can be seen as a particular case of the definition used in classical mechanics (2.1), was called exclusive, as it does not account for the interaction as part of the internal energy of the system ($E_{\mathrm{S}} = \mathcal{H}_0$) [45].

Another perspective to HB work is that it may still be interpreted as the mechanical work done *by the* system of interest S on external agents (systems) E, multiplied by -1, i.e. $\mathcal{W}_{\mathrm{HB}} = -\mathcal{W}_{\mathrm{S}\to\mathrm{E}}$. This perspective was described by Peliti, citing Gibbs[9] [17, 32]. In accordance with this view, HB work accounts for the energy *supplied by* S, and not that *delivered to* it, contrary to the perspective of mechanics (2.1). For weak interactions (when compared to the internal energies of E and S), HB work coincides with the mechanical work done by E on S, so that $-\mathcal{W}_{\mathrm{S}\to\mathrm{E}} = \mathcal{W}_{\mathrm{hb}} = \Delta\mathcal{H} \approx \Delta\mathcal{H}_0 = \mathcal{W}_{\mathrm{E}\to\mathrm{S}}$. This result may be the cause of great confusion when adapting thermodynamics to small systems: thermodynamics was primarily developed for macroscopic systems whose interaction terms are negligible when compared to the internal energies[10]. Therefore work is interchangeably treated as work done *on* the system of interest S by the outside E, $\mathcal{W}_{\mathrm{E}\to\mathrm{S}}$, or as the work done *by the* system of interest on the exterior multiplied by -1, $-\mathcal{W}_{\mathrm{S}\to\mathrm{E}}$. When work is adapted to small, strongly coupled, few-particle systems, this property does not persist, as the above discussion demonstrates[11].

It is important to highlight here the general character of the mechanical work when compared to the HB definition: throughout the whole discussion, the connections between work and internal energy are often deduced as a result of the definition of classical mechanics, and when the notion of force or displacement is somehow obscure, it is taken as a principle of mechanics. Consequently, HB work can be seen as a special case of the Work-Energy principle, in two different ways: either (i) assuming the interaction as part of the internal

[8] This interpretation is in fact in accordance with Gibbs' view of internal energy, as stated in the footnote of page 4 of [16].

[9] Peliti called these external agents as *steering bodies* and Gibbs describes them as *external bodies*. In fact, when looking at the usual definitions in classical thermodynamics, we see that in most cases, thermodynamic work refers to the transfer of energies from the system of interest to the environment that surrounds it. This interpretation was also implicitly considered in a quantum context, in the deduction of ergotropy (see Section 2.6 and [29, 30, 35]).

[10] However, the interaction is fundamental for the system to evolve to an equilibrium condition. See Section 2 of the [18] reference for more details.

[11] E.g. in a two-particle system where both particles interacts by means of a position dependent potential $\mathcal{V} \equiv \mathcal{V}(x_1, x_2)$, then we can check that $-d\mathcal{V} = -(\partial_{x_1}\mathcal{V})dx_1 - (\partial_{x_2}\mathcal{V})dx_2 = \mathcal{W}_{2\to1} + \mathcal{W}_{1\to2}$, so that $\mathcal{W}_{2\to1} = -\mathcal{W}_{1\to2}$, only if $dV = 0$.

energy or (ii) considering that the HB work is simply the negative of the mechanical work done by the system of interest and not on it. Nevertheless, interaction terms are not commonly treated as part of the internal energy in classical mechanics contexts and its inclusion as part of the internal energy overcast the clear meaning of the Work-Energy principle: work done *on* S will always be equal to the change in internal energy, clearly defined in Section 2.1 with no connection to external degrees of freedom whatsoever. When the notion of force and displacement is sufficiently clear, work will be computed as $\int f dx$ (Eq. (2.1)) and no further consideration is needed. Furthermore, taking Eq. (2.1), we can not only distinguish the contribution of each individual force to the total work but also compute work for systems whose Hamiltonian is not explicitly time dependent, a property not covered by the HB definition.

It could be argued that a classical parameter, explicitly dependent on time, must be considered to define work in the context of stochastic thermodynamics, since it is expected to be connected with macroscopic deterministic properties of the system. We show in the sequence, however, that there may be cases in which even the HB definition, if considered for general systems, does not capture forms of work in the sense of statistical physics.

2.4 Time-independent NFVs

As described in Section 2.2, when smaller systems are considered, care must be taken when defining the Non-Fluctuating Variables (NFVs), fundamental for the definition of work in a thermodynamic context. As we have seen, the most direct way adopted in the literature was to consider NFVs as explicitly time-dependent functions. However, there may be cases in which variables evolve with low fluctuations, as a consequence of the dynamics of the system as a whole, in order to be considered NFVs without necessarily demanding an explicit dependence on time. In these cases, there is a dynamically induced time-dependency instead of a parametric-induced one. In fact, even in the statistical physics treatment of macroscopic systems, explicitly time-dependent functions are not the only NFVs. As mentioned, an example is precisely the position of the piston confining a heated gas in Fig. 2.3. Therefore, already in the context of statistical physics, there are instances in which basing our notion of work only on explicitly time dependent NFVs leads us to a mistaken view of work. In order to avoid it, the Tolman Criterion was used as a guide.

Similarly, in the context of stochastic thermodynamics, we might find time independent NFVs, and HB definition does not capture useful forms of work that may emerge from it. To explicitly elucidate this point, we consider again a three-particle system whose dynamics is described by the classical hamiltonian function:

$$\mathcal{H} = \sum_{i=1}^{3} \frac{p_i^2}{2m_i} + \sum_{j>i=1}^{3} \mathcal{V}_{ij}\left(x_i - x_j\right). \tag{2.26}$$

Considering that the HB definition demands an explicit time dependence, a first step to be taken in order to describe a HB work is to obtain an effective Hamiltonian, explicitly dependent on time (making the system non-autonomous). Taking particle 3 as a controlled system, we assume that its position is an imposed function of time, $\lambda(t)$. If we directly employ the substitution $x_3 \to \lambda$ into the Hamiltonian (2.26), we get

$$\mathcal{H}_{\text{trial}}(t) = \sum_{i=1}^{2}\left(\frac{p_i^2}{2m_i} + \mathcal{V}_{i3}(x_i - \lambda(t))\right) + \mathcal{V}_{12}(x_1 - x_2) + \frac{m_3\dot{\lambda}^2(t)}{2}, \tag{2.27}$$

where the velocity of particle 3 and, therefore, its kinetic energy is also controlled, so that we can make the replacement $p_3^2/2m_3 \to m_3\dot{\lambda}^2(t)/2$. We call $\mathcal{H}_{\text{trial}}(t)$ as a trial Hamiltonian. If the HB work definition was considered for this Hamiltonian, then we would get

$$\mathcal{W}_{\text{hb}}(t,0) = \Delta\mathcal{H}_{\text{trial}} = \Delta\left[\sum_{i=1}^{2}\left(\frac{p_i^2}{2m_i} + \mathcal{V}_{i3}(x_i - \lambda(t))\right) + \mathcal{V}_{12}(x_1 - x_2) + \frac{m_3\dot{\lambda}^2(t)}{2}\right]. \tag{2.28}$$

Following the discussions of the previous section, HB formulation demands that work is the negative value of the work done *by* particle 2 and the interaction energy with external agents must be accounted as part of the internal energy. Moreover, both the kinetic term $\Delta m_3\dot{\lambda}^2(t)/2$ as well as the interaction with particle 1 $\Delta\mathcal{V}_{13}(x_1 - \lambda(t))$ should not appear in (2.28). This simple fact exposes an interesting feature of the HB definition when applied to small systems: interactions between the controllable acting system and the "bath" with which S interacts are commonly neglected, so terms like $\mathcal{V}_{13}(x_1 - \lambda(t))$ do not often appear. Also, note that the kinetic term $\Delta[m_3\dot{\lambda}^2(t)/2]$ can be seen as an analogous to $g(t)$ in Eq. (2.21), where now, the physical meaning is clear, as already anticipated by Peliti [32]. This term is commonly disregarded and it does not change the dynamics of the system of interest (see, for example, Eq. 7 of [94]). Neglecting these terms from our test Hamiltonian $\mathcal{H}_{\text{trial}}$, we can write a new effective Hamiltonian

$$\mathcal{H}_{\text{eff}}(t) = \sum_{i=1}^{2}\frac{p_i^2}{2m_i} + \mathcal{V}_{12}(x_1 - x_2) + \mathcal{V}_{23}(x_2 - \lambda(t)). \tag{2.29}$$

Notably, Eq. (2.29) can be written in the form (2.18), described earlier, such that

$$\mathcal{H}_{\text{eff}}(t) = \mathcal{H}'\left(x_2, p_2, \lambda\right) + \mathcal{V}_{\text{int}}(x_2, x_1) + \mathcal{H}_{\mathrm{E}}\left(p_1\right), \tag{2.30}$$

where $\mathcal{H}' = p_2^2/2m_2 + \mathcal{V}_{23}(x_2 - \lambda(t))$ refers to the *inclusive*-like internal energy of S, $\mathcal{V}_{\text{int}} = \mathcal{V}_{12}(x_1 - x_2)$ describes the interaction between S and the environment E and $\mathcal{H}_{\mathrm{E}} = p_1^2/2m_1$ corresponds to the energy of the environment. Computing the HB work for this system, we get

$$\mathcal{W}_{\text{hb}}(t,0) = \sum_{i=1}^{2}\Delta(p_i^2/2m_i) + \Delta\mathcal{V}_{12}(x_1 - x_2) + \Delta\mathcal{V}_{23}(x_2 - \lambda(t)) \tag{2.31}$$

As suggested by Jarzynski [88], $\mathcal{W}_{\mathrm{hb}}$ can be interpreted as both thermodynamic work done on particle 2 and thermodynamic work done on both particles 1 and 2.

Following an inclusive formulation, i.e. taking $\mathcal{H}'\left(x_2, p_2, \lambda\right)$ as internal energy and considering the first law of thermodynamics, we have that heat, defined by $\mathcal{Q}_{\mathrm{FH}} = \Delta\mathcal{H}' - \mathcal{W}_{\mathrm{FH}}$, can be written as[12]

$$\mathcal{Q}_{\mathrm{hb}}(t,0) = \int_0^t dt' \dot{x}_2 \frac{\partial \mathcal{H}'\left(x_2, p_2, \lambda_{t'}\right)}{\partial x_2} + \int_0^t dt' \dot{p}_2 \frac{\partial \mathcal{H}'\left(x_2, p_2, \lambda_{t'}\right)}{\partial p_2}. \tag{2.32}$$

From the Hamilton equations,

$$\mathcal{Q}_{\mathrm{hb}}(t,0) = -\int_0^t dt' \frac{\partial V_{12}\left(x_2 - x_1\right)}{\partial x_2} \dot{x}_2 = \mathcal{W}_{1\to 2}(t,0). \tag{2.33}$$

That is, heat obtained from (2.32) is equal to the mechanical work done by particle 1 on particle 2, therefore endorsing the example discussed in the beginning of Section 2.2. Moreover, it is not difficult to show that we would obtain similar results if an arbitrarily large number of particles N were considered instead of particle 1.

In order for the expression (2.33) to be unequivocally considered as heat in a thermodynamics basis, we must ensure that it cannot describe thermodynamic work. This cannot be guaranteed for every scenario. For example, we can assume a classical distribution ϱ for the three-particle system to be such that the position and velocity of particle 2 have extremely low fluctuations during a given time interval $[0, t]$ (as, for example, in cases which particle 2 is extremely heavy compared to the others). Therefore, for any instant in this interval, we have that $x_2 \approx \langle x_2 \rangle$, and $\dot{x}_2 \approx \langle \dot{x}_2 \rangle$ so that, according to the Tolman Criterion, x_2 and $\dot{x}_2$ can be taken as NFVs. Moreover, it follows $\langle \partial_{x_2} V_{i2}\left(x_2 - x_i\right) \dot{x}_2 \rangle \approx \langle \partial_{x_2} V_{i2}\left(x_2 - x_i\right) \rangle \langle \dot{x}_2 \rangle$. As a result, we get that

$$\langle \mathcal{Q}_{\mathrm{hb}}(t,0) \rangle \approx \int_C f_{x_2} dx_2, \tag{2.34}$$

where $dx_2 = \dot{x}_2 dt \approx \langle \dot{x}_2(t) \rangle dt$ and $f_{x_2} = -\langle \partial_{x_2} \mathcal{V}_{12}\left(x_2(t) - x_1(t)\right) \rangle$. Therefore, HB heat can, in addition to being seen as mechanical work, also have a form very similar to physical-statistical work $\mathcal{W}_{\mathrm{sp}}$: since the variable has low fluctuation and can be considered a NFV, it induces a format very similar to that of Eq (2.13), i.e. $\delta\mathcal{W}_{\mathrm{sp}} = f_{x_2} dx_2$. Similarly, it is possible to prove a similar result if we substitute particle 1 for N particles where one of N particles has low fluctuations. In Fig. 2.5(b), some possible microstates for particle systems are described, where particle 2 and one of the N particles, identified as 1, are heavy and have low fluctuations. These microstates are compared with the piston and gas (Fig. 2.5(a)) described earlier in Fig. 2.3. Note that the positions of particles 1 and 2 behave similarly to the position of the piston in Fig. 2.5(a) and, similarly to the piston case, no explicit time dependency was *imposed* on these NFVs.

It can be argued that the statistical physics definition of work, $\delta\mathcal{W}_{\mathrm{sp}}$, was formulated in a context where systems are close to equilibrium and additional assumptions are demanded.

[12] See Eqs. (7) and (8) from [88].

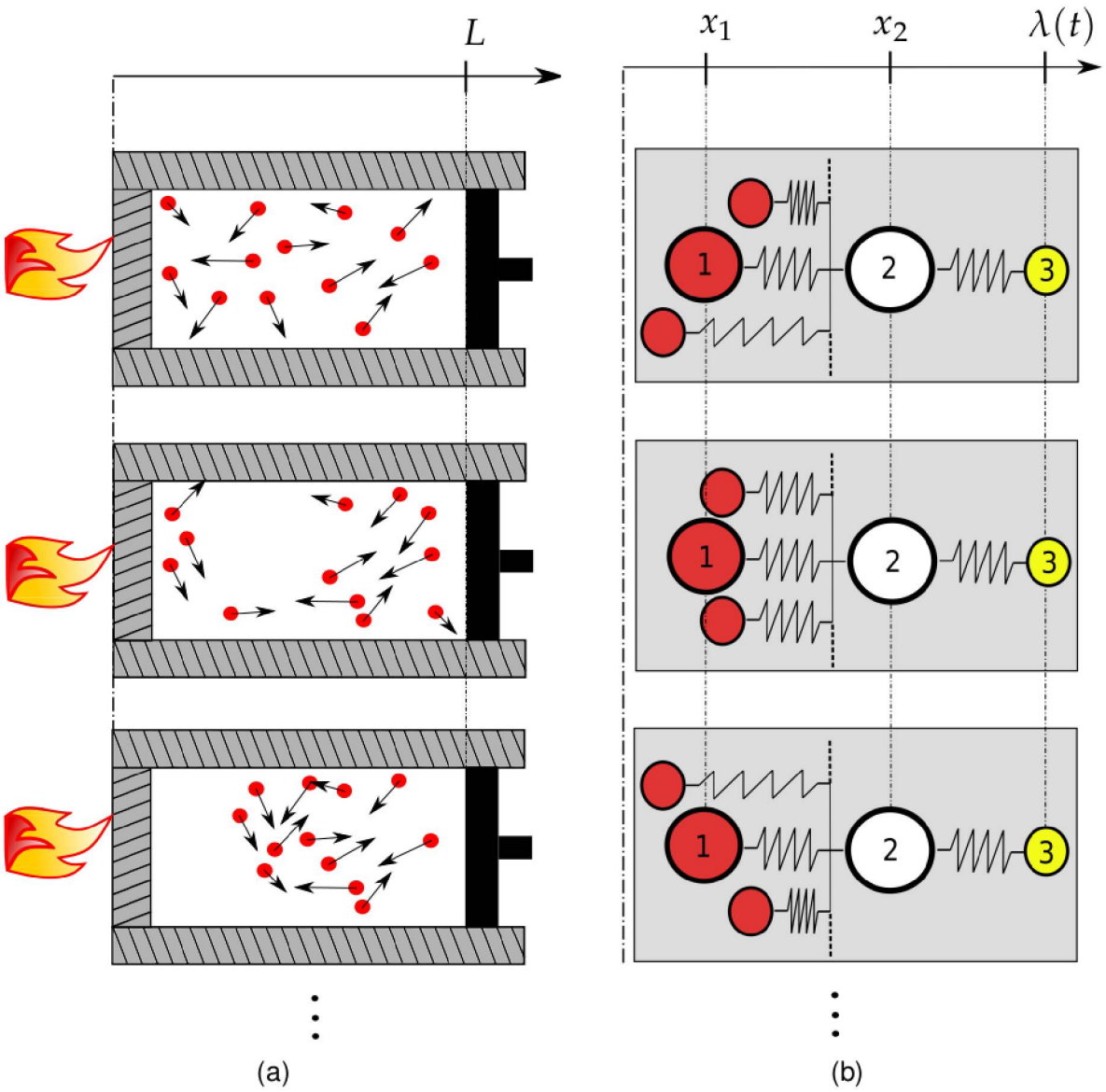


Figure 2.5 – External variables in general systems at a given instant of time t: (a) Some microstates of the piston+gas system, heated by a flame on the left side; the position L of the piston is approximately the same for each microstate of the system, satisfying Tolman's criterion with no explicit dependency assigned to it. (b) Some microstates of the many-particle system, where N of them interact with particle 2, and a time-dependent protocol $\lambda(t)$ is imposed to the position of particle 3, which also interacts with particle 2; particles 1 and 2 can have large enough masses when compared to the other particles, so that their positions and velocities practically do not fluctuate in the system; by Tolman's criterion, the positions and velocities of particles 1 and 2 can be taken as NFVs. Therefore, these variables can induce a form of work similar to a statistical-physics one, described in Eq. (2.13). On the other hand, these quantities are taken as heat when using a HB definition.

Indeed, in the context described here, such equilibrium hypotheses are not satisfied and therefore, even though $f_{x_2}dx_2$ in Eq. (2.34) has a form similar to $\delta\mathcal{W}_{\rm sp}$ and satisfies Tolman's criterion, one would still expect it to describe heat and not work. However, we must remind the reader that the statistical physics definition was constructed in order to mimic the thermodynamic concept of work which can be qualitatively understood as the form of energy transfer that takes place through a variable with trackable, predictable useful behavior.

Now, when we look at the term $f_{x_2}dx_2$, we see that it captures these essential features of thermodynamic work. Therefore, it does not seem physically consistent to us to call $f_{x_2}dx_2$ heat. In this sense, the HB definition, while consistent for many cases, does not capture this essence of work from thermodynamics in cases like the very special one described here.

Another point worth mentioning is that the HB definition was constructed primarily taking into account thermodynamics ingredients similar to those of statistical physics. Therefore, it is natural to expect that the HB definition does not describe $f_{x_2}dx_2$ as work, since distributions like the one we have considered are not encapsulated in the scope of stochastic thermodynamics. Though we agree with this statement, we are still compelled to ask: is it possible, in systems of few particles with general distributions, to describe useful work, in the sense of $\delta\mathcal{W}_{\rm sp}$? If we assume that this question cannot be answered by means of HB definitions, then we must turn to other possible directions. We believe we have a clue when looking to the form $f_{x_2}dx_2$ in Eq. (2.34).

2.5 Quantum thermodynamics work

The existence of a rigorous and precise definition of work in a quantum context has been intensely debated by the community. In view of the conclusions presented above, we have, at least, two forms of defining work, *viz.* a mechanical or thermodynamic approach. If we aim to adapt the concept of classical mechanics work to the quantum realm, two difficulties arise from the very beginning: both the notion of force and trajectory are not unequivocally established in quantum mechanics. Despite these difficulties, Prentis and Fedak [25] presented a mechanical notion of quantum work. In their research, they identified a work operator (see section IV of [25]), deducing a relation accounted as a law of conservation of energy in the sense of (2.3), so as to relate the kinetic energy variation of a particle with work done on it, in terms of Heisenberg operators. However, it is not clear how the formalism proposed can be extended to N-particle systems, so as to identify a general notion of work in the sense of (2.5), where the Work-Energy principle can be deduced. Moreover, the form of the work operator proposed by the authors is such that its "classical-like" part, written as the product FP of the the force F and momentum P operators, is not necessarily Hermitian. Therefore, it is not clear, in cases in which FP is non-Hermitian, what is its exact physical meaning. Their approach is thus incomplete and cannot encompass the basic features of mechanical work.

As the approach in [25] is the only, to our knowledge, that presents an essentially *mechanical* notion on a quantum context, we conclude that a mechanical notion is still an open subject. On the other hand, a wide range of quantum thermodynamics definitions of work was presented in the literature. Throughout the rest of this section, we review some of the definitions known to date pointing out their peculiarities.

2.5.1 Hamiltonian-based definition

We consider in this and in the following subsection, a preparation ρ_{S} of a system S acting on a Hilbert space $\mathbb{H}_{\mathrm{S}}$. Furthermore, we assume that the system evolves in accordance with an explicitly time-dependent Hamiltonian operator $H_{\mathrm{S}}^{\mathfrak{s}} \equiv H_{\mathrm{S}}^{\mathfrak{s}}(\lambda(t)) \equiv H_{\mathrm{S}}^{\mathfrak{s}}(t)$, by means of a unitary evolution operator U_t. Additionally, we introduce the notation in which all the Schrödinger operators are represented by $A^{\mathfrak{s}}$ while the superscript is dropped for the Heisenberg version A.

In this context, the HB definition of work, previously introduced in a context of classical stochastic thermodynamics, was naturally adapted to Quantum Thermodynamics [19, 21, 28–38]: given the Hamiltonian $H_{\mathrm{S}}^{\mathfrak{s}} \equiv H_{\mathrm{S}}^{\mathfrak{s}}(\lambda(t)) \equiv H_{\mathrm{S}}^{\mathfrak{s}}(t)$ referring to the internal energy of the system of interest S, then HB work W_{hb} is defined as

$$\delta W_{\mathrm{hb}} = \mathrm{Tr}_{\mathrm{S}}(\rho_{\mathrm{S}} \partial_t H_{\mathrm{S}}^{\mathfrak{s}}(t)) dt. \tag{2.35}$$

We notice, once again, the utility or deterministic "flavor" of the HB work: once a classical variable λ that evolves deterministically is imposed, work is then related to λ. Heat Q_{hb}, on the other hand, is related to the temporal variation of the density operator $\rho_{\mathrm{S}}(t)$

$$\delta Q_{\mathrm{hb}} = \mathrm{Tr}_{\mathrm{S}}((\partial_t \rho_{\mathrm{S}}) H_{\mathrm{S}}^{\mathfrak{s}}(t)) dt. \tag{2.36}$$

It is important to remark that since the quantum HB definition can be seen as an adaptation of the classical HB form, the questionings raised in the classical scenario can also be raised here. Moreover, as we move to the quantum realm, other difficulties may appear, which we treat next.

2.5.2 Work statistics?

How can we describe mean values of functions or statistical moments of work in a quantum context? For instance, can we deduce Jarzynski's equaliity (Eq. (2.20)) in the quantum realm? One of the forms in which work as a stochastic variable was inferred is by means of the so-called two-point measurement (TPM) protocol [21, 31, 65], schematically represented in Fig. 2.6. TPM is often applied under the following conditions: after being prepared at $t = 0$ in a generic state ρ_{S}, the system is submitted to a projective measurement of energy at t_1, thus jumping to an $H_{\mathrm{S}}^{\mathfrak{s}}(t_1)$ eigenstate $|e_n\rangle$ with probability $\mathfrak{p}_n = \langle e_n|\rho_{\mathrm{S}}|e_n\rangle$. The system then evolves unitarily (via $U_{\Delta t}$, with $\Delta t = t_2 - t_1$) until the instant t_2, when a second measurement is performed and a random eigenvalue ε_m of $H_{\mathrm{S}}^{\mathfrak{s}}(t_2)$ is obtained with probability $\mathfrak{p}_{m|n} = |\langle \varepsilon_m| U_{\Delta t} |e_n\rangle|^2$. In this run of the experiment, work is computed as $w_{mn} = \varepsilon_m - e_n$. After many runs, the probability density associated with work is built as $\wp_w = \sum_{mn} \mathfrak{p}_{m|n}\, \mathfrak{p}_n\, \delta_{\mathrm{D}}(w - w_{mn})$, where δ_{D} is the Dirac delta function and $\int dw\, \wp_w = 1$. It follows that the k-th moment of work can be evaluated as $\overline{w^k} = \int dw\, \wp_w w^k = \sum_{mn} \mathfrak{p}_{m|n} \mathfrak{p}_n w_{mn}^k$.

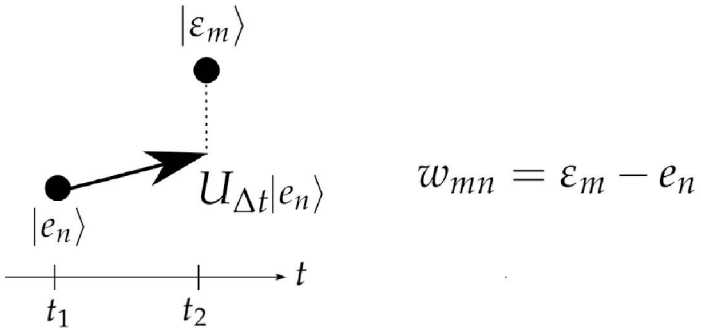


Figure 2.6 – Schematic representation of a round of the two-point-measurement (TPM) protocol. The system is initially ($t = t_1$) submitted to a projective measurement of energy, jumping to an $H_{\mathrm{S}}^{\mathrm{s}}(t_1)$ eigenstate $|e_n\rangle$. The system then evolves unitarily ($U_{\Delta t}$, continuous line) until the instant t_2, when a second measurement is performed and collapsing to $|\varepsilon_m\rangle$, an eigenstate of $H_{\mathrm{S}}^{\mathrm{s}}(t_2)$ (dashed line). Work in this round of the experiment is then computed as the difference $w_{mn} = \varepsilon_m - e_n$.

From distributions $\wp_w$ with work seen as a stochastic variable, the TPM scheme has enabled the experimental validation of important classical fluctuation theorems in a quantum context (see, for example, Refs. [21, 65, 97] and references therein). Moreover, it gives a relatively simple and fairly general way of accounting for work statistics in the quantum thermodynamics domain. For instance, a quantum form of Jarzynski equality is directly obtained from the TPM distribution $\wp_w$: given an initial Boltzmann-Gibbs state $\rho_{\mathrm{S}}(0) = \mathrm{e}^{-\beta H_{\mathrm{S}}(0)}/\mathcal{Z}_0$, with the two measurements taking place at $t_1 = 0$ and $t_2 = t$, we deduce Jarzynski relation

$$\int_w \wp_w \exp(-\beta w) dw = \mathcal{Z}_t/\mathcal{Z}_0, \tag{2.37}$$

where once again $\mathcal{Z}_t = \mathrm{Tr}\,\mathrm{e}^{-\beta H^S(t)}$ refers to the partition function.

It is important to highlight, though, that what is directly measured in a TPM protocol is energy, not work. Therefore, the usefulness of Jarzynski equality can be questioned when using TPM protocol, as one might determine $\mathcal{Z}_t$ directly from energy measurements, without the need of the equality. This point was raised in [60], where the authors presented an alternative way of measuring work without the need of energy measurements.

It is also worth mentioning that the application of the TPM protocol to thermodynamic contexts typically presumes initial states such that $[\rho_{\mathrm{S}}(0), H_{\mathrm{S}}^{\mathrm{s}}(0)] = 0$ [21, 65, 97]. In fact, due to this feature, TPM was recently challenged when compared with HB definition by Perarnau-Llobet et al. in [37]. The authors showed that there is no general process-dependent measurements (see Chapter 4) that satisfy both of the following hypotheses simultaneously: (i) for any state ρ_{S}, the mean value relation $\langle W\rangle = \langle H_{\mathrm{S}}(t)\rangle - \langle H_{\mathrm{S}}(0)\rangle$ is valid and (ii) the work statistics matches the TPM protocol statistics whenever $[\rho_{\mathrm{S}}(0), H_{\mathrm{S}}^{\mathrm{s}}(0)] = 0$. With that, an obstacle is already seen when regarding both HB work and TPM protocol, since one expects (i) to hold given the HB definition (Eq. (2.35)), but (ii) to be valid for a TPM protocol.

A form of computing work statistics alternative to TPM was proposed in the literature as

well: by noting that the HB work can be written as

$$W_{\mathrm{hb}}(t,0) = \mathrm{Tr}\left[\rho_{\mathrm{S}}(t)H_{\mathrm{S}}^{\mathrm{s}}(t)\right] - \mathrm{Tr}\left[\rho_{\mathrm{S}}(0)H_{\mathrm{S}}^{\mathrm{s}}(0)\right] = \mathrm{Tr}\left[\rho_{\mathrm{S}}(H_{\mathrm{S}}(t) - H_{\mathrm{S}}(0))\right], \tag{2.38}$$

where we remind the reader that $H_{\mathrm{S}}(t) = U_t^{\dagger}H_{\mathrm{S}}^{\mathrm{s}}(t)U_t$ is the Heisenberg version of the Schrödinger operator $H_{\mathrm{S}}^{\mathrm{s}}(t)$, it is reasonable to define $W(t,0) = H_{\mathrm{S}}(t) - H_{\mathrm{S}}(0)$ as a quantum work observable, so that work statistics can be raised using the usual formalism of quantum mechanics. Therefore, the average value of a smooth function g (possibly a power $W(t,0)$) can be computed as $\mathrm{Tr}\left[\rho_{\mathrm{S}}\, g(W(t,0))\right]$. In principle, it seems that there is no objection to the idea of treating work as an observable. Indeed, an *observable* is technically a Hermitian operator whose set of eigenvectors spans the vector space, which $W(t,0)$ can be proved to be (see Appendix A). Although there are proposals defending this idea [30, 60–62], it has been an object of intense discussion and it remains unsettled [21, 31, 57, 63, 64].

Some authors argue that because work is related to a process rather than a system state variable, then a single measurement at a given instant of time cannot completely characterize it. This idea is explicitly stated by Campisi, Talkner, and Hänggi [21]:

"(...) work characterizes a process, rather than a state of the system; this is also an obvious observation from thermodynamics: unlike internal energy, work is not a state function (its differential is not exact). Consequently, work cannot be represented by a Hermitian operator whose eigenvalues can be determined in a single projective measurement. In contrast, the energy $H(\lambda_t)$ ... must be measured twice, first at the initial time $t = 0$ and again at the final time $t = \tau$."

To a certain extent, such a view departs from the idea encoded in the quantum axiom which states that [98] "every measurable physical quantity $\mathscr{A}$ is described by an operator acting in $\mathbb{H}$; this operator is an observable". In other words, if work is to be taken as a *measurable* physical quantity, then some quantum observable must be assigned to it. On the other hand, in response to that, it can be argued that this quantum axiom does not elucidate the precise meaning of measurable, especially whether the quantity under scrutiny has to be *directly* accessed in a lab experiment or indirectly, by means of measurements of another observable correlated to it. Moreover, the axiom does not give information with respect to two-time quantities such as work, displacement, and velocity, which cannot be accessed by only one measurement at an instant of time.

In another vein [31, 37, 65], it has been shown that TPM statistics results are different from those of work observable. For instance, in general, Jarzynski relation cannot be verified when assuming work as an observable, that is,

$$\mathrm{Tr}\left[\rho_{\mathrm{S}}(\exp(-\beta(H_{\mathrm{S}}(t) - H_{\mathrm{S}}(0))))\right] \neq \frac{\mathcal{Z}(t)}{\mathcal{Z}(0)}, \tag{2.39}$$

even though an initial Boltzmann-Gibbs state is considered. Therefore, taking FTs as fundamental premises favors the TPM protocol [31], to the detriment of operator-based formulations. However, despite the demonstrated relevance of FTs in classical stochastic

thermodynamics, they are not expected to be valid in general quantum contexts in the same classical form, so that a work operator should not be automatically discarded for not leading to the usual FTs, as pointed out in [63]. On the other hand, in the same reference, a scenario is presented in which a system is prepared in an eigenstate of work while the energies at different instants of time are uncertain: given a work operator eigenstate $|w=0\rangle$ with eigenvalue 0, it can be deduced that $\langle W(t,0)\rangle = 0$ and $\sigma_W = \sqrt{\langle W^2(t,0)\rangle - \langle W(t,0)\rangle^2} = 0$, while $\langle H_S^n(t)\rangle \neq \langle H_S^n(0)\rangle$ for a given power of n. This led the author to conclude the following:

"Thus, according to this definition it is possible to have energy exchange with strictly zero fluctuations of work. In other words, the link between energy exchange and the work done on a thermally isolated system is generally absent".

In another line of reasoning, it was stated in [33] that:

"As the number of possible values of work $w = \varepsilon_m - \epsilon_n$ is typically larger than the dimension of the space of states, a Hermitian operator representing work cannot exist."

However, if we take the difference $C = A - B$ of any quantum observables A and B as an observable as well, then the eigenvalues of C will not necessarily be the same as the difference of the eigenvalues of A and B. In other words, denoting c_i as the eigenvalues of C, it is not always true that $c_i = a_j - b_k$, where $a_j(b_k)$ are eigenvalues of $A(B)$. Indeed, even if we consider, for example, the case of a spin of a particle in the direction x and y, S_x and S_y, we can check that[13] the difference between the eigenvalues of S_x and S_y have three possible outcomes 0, $\hbar$, and $-\hbar$, while the eigenvalues of $S_x - S_y$ are $\pm\frac{\hbar\sqrt{2}}{2}$. Now, turning back to work, we can conclude that assuming work as an observable implies to admit that its eigenvalues are not necessarily $\varepsilon_m - \epsilon_n$, i.e. the difference in the eigenvalues of the energies $H_S(t)$ and $H_S(0)$. Despite arguably odd from a classical perspective, all these results are reasonable in a quantum formalism.

Given the aforementioned difficulties, it is fair to conclude that the correct way of raising work statistics in a quantum context is still an open matter. Indeed, many approaches have been presented suggesting alternative paths. For instance, schemes for measuring work other than TPM protocols exist in which only one (generalized) quantum measurement is needed [33, 60]. Also, the so-called Bayesian networks have been regarded, so that a work estimator was inferred from the very statistical description of the system [70] and fluctuation relations were deduced not only for work but also to other physical quantities [71]. The possibility of considering quasi-probabilities and the role of contextuality has been considered in [69]. In another perspective, ways of avoiding the invasiveness nature of a TPM first measurement has been considered in [59, 60, 99].

Finally, it is important to point out that the difficulties of collecting work statistics are mainly related to the fact that we do not have a clear recipe for describing interval-dependent

[13] For more details on these computations, see Subsection 3.2.4.

quantities in quantum mechanics. In fact, if we were to consider linear or angular displacements, changes in energy, or any other interval-dependent physical quantity, we would be drawn into many of the aforementioned discussions as well. For example, it is not clear how we can raise the statistics of the displacement of a free particle: should we consider a TPM perspective or a displacement quantum observable? Can we consider an alternative way to statistically describe displacement in quantum mechanics? These questions will be answered posteriorly.

2.5.3 Work and autonomous systems

We consider now a state ρ acting on a bipartite Hilbert space $\mathbb{H} = \mathbb{H}_{\mathrm{S}} \otimes \mathbb{H}_{\mathrm{E}}$ representing a system of interest S interacting with an external system E (possibly a bath, an ancilla, or any other system). Furthermore, the whole universe $\mathrm{U} = \mathrm{S} + \mathrm{E}$ evolves unitarily U_t and we denote $\rho_{\mathrm{S(E)}} = \mathrm{Tr}_{\mathrm{E(S)}}\, \rho$ the reduced state of part $\mathrm{S(E)}$. Given this prescription, two strategies are most widely employed to define work and heat transferred to S.

One of them [5, 52–54, 100] consists of taking two subsystems of E as reservoirs of work (battery) and heat, so that the energy of the system as a whole is described by a general Hamiltonian $H = H_{\mathrm{S}} + H_{\mathrm{W}} + H_{\mathrm{Q}} + V_{\mathrm{SW}} + V_{\mathrm{SQ}}$ where H_{S} refers to the energy of the system of interest, $H_{\mathrm{Q(W)}}$ is the energy of the heat (work) reservoir and $V_{\mathrm{SQ(SW)}}$ accounts for the interaction between the corresponding reservoir and the system of interest. In such cases, all energy flowing to (from) the work (heat) reservoir is taken as work (heat). Therefore, distinguishing work from heat becomes equivalent to differing work from heat reservoirs. In the approaches presented so far in the literature, this distinction is clear due to direct analogies with equilibrium thermodynamics. For instance, in [54], the heat reservoir is described by a large number of systems at a fixed temperature, whereas the battery is described by a Hamiltonian $H_{\mathcal{W}} = mgX$ representing a weight-like potential energy.

Nevertheless, the generalization of reservoir-based approaches can be jeopardized due to the lack of an explicit criterion distinguishing a work reservoir from a heat reservoir. For example, we could consider the quantum analogue of the three-particle system described in Eq. (2.2), i.e., $H = \sum_{i=1}^{3} P_i^2/2m_i + \sum_{j>i=1}^{3} V_{ij}\left(\mathrm{X}_i - \mathrm{X}_j\right)$, where the operators X_i and P_i are the operators corresponding to the positions and momenta of the particles. Now, we could again take the system of interest as particle 2, so that it is not trivial to characterize either particles 1 or 3 as work or heat reservoir *for general initial states*. Indeed, when considering systems initially in equilibrium or Gibbs-Boltzmann states for one of the systems, it is natural to take the respective system as a heat reservoir. However, when we are looking for more fundamental, primitive and microscopic approaches to the definition of work and heat, we can ask ourselves: is it possible to define heat or thermodynamic work when considering general states, not necessarily those of thermal equilibrium? How?

Another strategy to define work and heat for autonomous systems can be described as follows [42–44, 101]: defined the system of interest S, the evolution of the reduced state of

the system of interest can be written as

$$\partial_t \rho_{\mathrm{S}}(t) = \frac{[H_u^{\mathrm{s}}, \rho_{\mathrm{S}}]}{i\hbar} + \mathcal{D}\rho_{\mathrm{S}}(t) \tag{2.40}$$

where $H_u^{\mathrm{s}}(t)$ is the operator related to the unitary part of the evolution and the superoperator $\mathcal{D}$ is a dissipator acting on $\rho_{\mathrm{S}}(t)$; work is then computed, in a similar form as HB, as

$$\delta W_{\mathrm{un}} = \mathrm{Tr}\left[\rho_{\mathrm{S}}(t)\partial_t H_u^{\mathrm{s}}(t)\right] dt. \tag{2.41}$$

Heat is then defined as

$$\delta Q_{\mathrm{un}} = \mathrm{Tr}\left[(\partial_t \rho_{\mathrm{S}}(t))H_u^{\mathrm{s}}\right] dt. \tag{2.42}$$

When considering this strategy, extra assumptions are usually imposed on the correlations and interactions between S and E (Born-Markov hypothesis, for example [102]). However, such hypotheses have been recently dropped and new interesting proposals have been addressed in the literature, where Eqs. (2.41) and (2.42) or adaptations of them were considered. For instance, work and heat were computed for a strongly correlated dipole in [43]. Also, work resulting from initial coherences was analyzed using collisional models in [44].

Despite effective and relevant, the approaches via Eqs. (2.41) and (2.42) lead us to ambiguities when we aim at a generalization of the notions of heat and work. Consider a simple system of two particles interacting via elastic potential, evolving in accordance with the Hamiltonian $H = \sum_{i=1}^{2} P_i^2/2m_i + \frac{k}{2}(X_2 - X_1)^2$. We assume a general initial state ρ and select particle 1 as our system of interest S and particle 2 as the exterior E. The evolution of the reduced state ρ_{S} can be deduced by taking the partial trace on the Liouville-von Neumman Equation [40, 103],

$$\partial_t \rho(t) = \frac{1}{i\hbar}\left[H, \rho(t)\right], \tag{2.43}$$

so as to obtain

$$\partial_t \rho_{\mathrm{S}}(t) = -\frac{[\rho_{\mathrm{S}}(t), (P_1^{\mathrm{s}})^2/2m_1 + \frac{k}{2}(X_1^{\mathrm{s}})^2]}{i\hbar} + \frac{\mathrm{Tr}_{\mathrm{E}}([\rho(t), \frac{k}{2}\{X_1^{\mathrm{s}}, X_2^{\mathrm{s}}\}])}{i\hbar}. \tag{2.44}$$

The unitary portion of the evolution will usually be related with external degrees of freedom, a feature disputed by advocates of the exclusive formulation. Furthermore, we expect that a work definition in a quantum context will converge to its classical analogue when treated in a semi-classical limit (when it exists). To test this limit, consider a localized distribution with negligible correlations so that the total quantum state is described approximately as $\rho(t) \approx \rho_{\mathrm{S}}(t) \otimes \rho_{\mathrm{E}}(t)$ during a short period, such that the relation $\mathrm{Tr}_2\left[\rho(t), \left\{X_1^{\mathrm{s}}, X_2^{\mathrm{s}}\right\}\right] \approx 2\left[\rho_{\mathrm{S}}(t), X_1^{\mathrm{s}}\langle X_2(t)\rangle\right]$ is satisfied. The state evolution equation then acquires the form

$$\partial_t \rho_{\mathrm{S}}(t) = -\frac{\left[\rho_{\mathrm{S}}(t), (P_1^{\mathrm{s}})^2/2m_1 + \frac{k}{2}\left((X_1^{\mathrm{s}})^2 - 2X_1^{\mathrm{s}}\langle X_2(t)\rangle\right)\right]}{i\hbar} \tag{2.45}$$

such that, using the notation in Eq. (2.40), $H_u^{\mathrm{s}} = (P_1^{\mathrm{s}})^2/2m_1 + \frac{k}{2}\left((X_1^{\mathrm{s}})^2 - 2X_1^{\mathrm{s}}\langle X_2(t)\rangle\right)$ and $\mathcal{D} = 0$. Work, from (2.41), is then

$$W_{\mathrm{u}} = \int_0^t \mathrm{Tr}\left(\rho_{\mathrm{S}}\partial_t H_u^{\mathrm{s}}\right) dt = -\frac{k}{2}\int_0^t \mathrm{Tr}\left(\rho_{\mathrm{S}} 2X_1^{\mathrm{s}}\partial_t\langle X_2(t)\rangle\right) dt. \tag{2.46}$$

This result does not converge to the variation of the internal energy of the system either for an exclusive or inclusive perspective in a semi-classical limit. With respect to the exclusive approach, work should equal the change in kinetic energy of particle 1 (the so-called bare Hamiltonian), $\langle P_1^2\rangle/2m_1$, which is clearly not the case. Regarding the latter, the change in internal energy must contain the interaction term, so the form of H_u^{s} should be $(P_1^{\mathrm{s}})^2/2m_1 + k(X_1^{\mathrm{s}} - 2X_1^{\mathrm{s}}\langle X_2(t)\rangle + \langle X_2^2(t)\rangle)/2$, and

$$\partial_t H_u^{\mathrm{s}} = \frac{k}{2}\left(-2X_1^{\mathrm{s}}\partial_t\langle X_2(t)\rangle + \partial_t\langle X_2^2\rangle\right). \tag{2.47}$$

The no-show of $\partial_t\langle X_2^2(t)\rangle$ in Eq. (2.46) can be directly traced back to the fact that $\langle X_2^2\rangle$ commutes with ρ_{S}, so that this term has been neglected in the formulation. Although this problem could easily be solved just by adding or subtracting terms to H_u^{s}, a criterion must be formalized such that the most physically consistent form of H_u^{s} is considered.

As much as changes has been done on Eq. (2.41) in order to take into account correlations [52, 56] and alternative approaches have been presented analyzing general quantum systems [66–68], there are still doubts about a general criterion to fundamentally describe internal energy and work in quantum autonomous scenarios. Moreover, it is still not quantitatively clear how the state of the system that does work (for example, particle 1 and 3) on the system of interest S (particle 2) changes the predictions of work. Also, even though it has been proposed forms of describing fluctuation theorems in the autonomous scenarios [67, 68], it is still elusive how they can be accounted when non-trivial states are considered for few-particles, strongly-interacting microscopic scenarios.

We close at this point the part of this chapter in which we review and investigate the main features of definitions of work in both quantum and classical scenarios. In the following sections, we treat other topics and concepts that surrounds work.

2.6 Bounds on thermodynamics work and ergotropy

We analyze here forms in which thermodynamics work is frequently bounded. Let us consider initially an usual equilibrium thermodynamics scenario: a system of interest S immersed in a bath B with temperature T and constant pressure, interacting with an external system A which is thermically isolated from both S and E. The first law applied to the system S can be written as

$$dE_{\mathrm{S}} = -\delta W_{\mathrm{S}\to\mathrm{A}} + \delta Q_{\mathrm{B}\to\mathrm{S}} \tag{2.48}$$

where, $-\delta W_{\mathrm{S}\to\mathrm{A}}$ is the work done *by* the system S on A[14], and $\delta Q_{\mathrm{B}\to\mathrm{S}}$, is heat flowing *from* the bath *to* the system. The second law holds in the sense that the total variation of entropy of the system S is given by

$$dS_{\mathrm{S}} = dS_{\mathrm{f}} + dS_{\mathrm{p}} \tag{2.49}$$

where

$$dS_{\mathrm{f}} = \frac{\delta Q_{\mathrm{B}\to\mathrm{S}}}{T} \tag{2.50}$$

is the flux of entropy from the bath to the system and

$$dS_{\mathrm{p}} \geq 0 \tag{2.51}$$

is the entropy production [2, 96]. Considering Eqs.(2.48)-(2.51), we have that

$$dS_{\mathrm{p}} = dS_{\mathrm{S}} - \frac{\delta Q_{\mathrm{B}\to\mathrm{S}}}{T} = dS_{\mathrm{S}} - \frac{dE_{\mathrm{S}} + \delta W_{\mathrm{S}\to\mathrm{A}}}{T} \geq 0. \tag{2.52}$$

For a positive temperature, we can rewrite the above equation as

$$TdS_{\mathrm{S}} - dE_{\mathrm{S}} - \delta W_{\mathrm{S}\to\mathrm{A}} \geq 0 \implies \quad \delta W_{\mathrm{S}\to\mathrm{A}} \leq -dF_{\mathrm{S}} \tag{2.53}$$

where $F_{\mathrm{S}} = E_{\mathrm{S}} - TS_{\mathrm{S}}$ is defined as the free energy related to S.

Relation (2.53) is a well-known result in the literature and can be regarded as an alternative form of stating the second law [20, 93, 95, 96, 104]. In fact, we can use the bound (2.53) to obtain the maximum possible work extraction $W_{\max}$, i.e. the maximum value $W_{\mathrm{S}\to\mathrm{A}}$ can take for any given initial configuration. By noticing that work cannot be greater than $F_i - F_{\min}$, with F_i and $F_{\min}$ being the initial and minimal value of F_{S} respectively, all we need to do is find out $F_{\min}$. There are many routes to prove that this minimum is achieved when S reaches a thermal equilibrium state with temperature T (see [29] and references therein).

It is worth highlighting here that Eq. (2.53) is valid as far as the notions of heat, work, entropy and entropy production are well-defined and Eqs.(2.48)-(2.51) applies. Therefore, even though forms of extending it to non-equilibrium quantum scenarios have been presented in [20, 95, 96], we cannot ensure their validity for general contexts since not only the very notion of work is debatable (as we have seen so far) but also those of entropy production, heat, and entropy itself [38]. Indeed, one may ask whether there are possibilities to deduce bounds for general quantum-mechanical instances in which not necessarily a bath, constant pressure or other thermodynamics ingredients are demanded. In the seminal work [29], Allahverdyan, Balian, and Nieuwenhuizen took an important step in this direction: they obtained a measure of the maximum extractable work of a quantum system submitted to an arbitrary unitary dynamics in a finite-dimensional Hilbert space; they named it *ergotropy*, which we succinctly discuss now.

[14] We considered here the usual regime of thermodynamics, in which the interactions are weak and $-W_{\mathrm{S}\to\mathrm{A}} \approx W_{\mathrm{A}\to\mathrm{S}}$. In this direction, we refer the reader to Subsection 2.3.

Consider a time-dependent Hamiltonian $H_{\mathrm{S}}^{\mathrm{s}}(t)$ describing the energy and the dynamics of a system S, where the time dependence encodes the effect of an external classical agent A on S. Moreover, consider a cyclic unitary process where $H_{\mathrm{S}}^{\mathrm{s}}(0) = H_{\mathrm{S}}^{\mathrm{s}}(\tau)$, i.e. after an interval τ the Hamiltonian is the same as $H_{\mathrm{S}}^{\mathrm{s}}(0)$ and the initial state $\rho_{\mathrm{S}}(0)$ evolves unitarily to $\rho_{\mathrm{S}}(t) = U_t \rho_{\mathrm{S}}(0) U_t^\dagger$. Considering that the maximum work *extracted* from S is aimed, the definition of HB work was used, taking into account the relation $W_{\mathrm{S}\to\mathrm{A}} = -W_{\mathrm{HB}} = -\int_0^\tau \mathrm{Tr}\left[\rho_{\mathrm{S}}(t)\partial_t H_{\mathrm{S}}^{\mathrm{s}}(t)\right] dt = \langle H\rangle_0 - \langle H\rangle_\tau$. By minimizing $\langle H\rangle_\tau$ over all possible unitary cyclic processes, it was showed in [29] that the stationary conditions are such that $[\rho_{\mathrm{S}}(\tau), H_{\mathrm{S}}^{\mathrm{s}}(0)] = 0$, so that the maximum extractable thermodynamic work W_{erg} done by S on A, *viz. ergotropy*, is

$$W_{\mathrm{erg}} = \max_U [W_{\mathrm{S}\to\mathrm{A}}] = \sum_{j,k} r_k \varepsilon_j (|\langle r_j|\varepsilon_j\rangle|^2 - \delta_{jk}), \tag{2.54}$$

where δ_{jk} is the Kronecker delta and r_k, $|r_k\rangle$ and ε_j are respectively the eigenvalues of $\rho_{\mathrm{S}}(0)$ and $H_{\mathrm{S}}^{\mathrm{s}}(\tau)$, ordered as $r_1 \geq r_2 \geq \cdots$ and $\varepsilon_1 \leq \varepsilon_2 \leq \cdots$.

Eq. (2.54) can be interpreted in a simple way. Given a arbitrary initial state ρ_{S} for a system of interest S, its initial average energy is $\sum_{j,k} r_k \varepsilon_j |\langle r_j|\varepsilon_j\rangle|^2 = \langle H\rangle_0$. In order to "extract" the maximum work from S, its final energy must be as little as possible; given the stationary conditions, the minimum of the final energy will occur when the lowest energy eigenstates obtain the highest populations.

It was also demonstrated in [29] that $W_{\mathrm{max}} = \Delta F \geq W_{\mathrm{erg}}$, that is, ergotropy will never be greater than the thermodynamics (reversible) limit W_{max}. Recently, interesting connections have been identified between correlations of bipartite systems and ergotropy [35, 105]. In fact, since ergotropy is related to unitary processes, and therefore processes without von Neumann entropy changes, it has also been related to the maximum thermodynamical work that one can extract in a open quantum dynamics context as well [106].

Given the importance of (2.53) and (2.54) to thermodynamics scenarios, we may ask ourselves whether other bounds can be deduced for general quantum autonomous scenarios as well, under *mechanical* lenses. To our knowledge, no such a limit was deduced in the literature.

2.7 Conservation of energy and the role of measurements

Conservation laws are known to impose restrictions to physical processes. Indeed, they are in accordance with our understanding of the physical world in which no creation nor vanishing of conserved quantities, such as energy, linear and angular momentum, takes place. They are well-established in classical autonomous contexts and their validity can be deduced even though distributions are considered. For instance, consider a universe described by a time-independent classical hamiltonian function

$$\mathcal{H} = \mathcal{H}_{\mathrm{S}} + \mathcal{H}_{\mathrm{R}}, \tag{2.55}$$

where S is a system of interest and $\mathcal{H}_{\mathrm{R}}$ refers to the energy of the rest of the universe U, possibly accounting for example interaction terms as well as bare Hamiltonian of an environment ($\mathcal{H}_{\mathrm{R}} = \mathcal{V}_{\mathrm{SE}} + \mathcal{H}_{\mathrm{E}}$), an ancillary system, or even a measurement apparatus. We could describe the conservation of energy as follows: given that an amount Δ of energy is transferred to S, then $\mathcal{H}_{\mathrm{R}}$ is expected to change an amount $-\Delta$ and vice-versa. Moreover, if we consider an initial distribution ϱ over the phase space for the whole system, then we can also derive[15] the fact that the probability $\wp_{\mathrm{S}}(\Delta, t_2, t_1)$ of Δ flowing to S during a given interval $[t_1, t_2]$ equals the probability $\wp_{\mathrm{R}}(-\Delta, t_2, t_1)$ of flowing $-\Delta$ from R, i.e.

$$\wp_{\mathrm{S}}(\Delta, t_2, t_1) = \wp_{\mathrm{R}}(-\Delta, t_2, t_1) \tag{2.56}$$

Furthermore, the distributions $\wp_{\mathrm{S(R)}}(\Delta, t_1, t_2)$ can, in principle, be inferred experimentally from measurements of energy of $\mathrm{S(R)}$ at times $t_{1,2}$. Since $\mathcal{H}_{\mathrm{R}}$ can account for the energy of an apparatus and its interaction with S, the energy transferred by a classical apparatus can in principle be estimated.

On the other hand, in the quantum world not only the validity of conservation laws is still under dispute [77, 79, 107–110], but also, the amount of exchange of energy and information with the apparatus [76, 78, 82–84, 86].

One of the main challenges in validating conservation laws in general quantum contexts comes from the irreducible disturbance provided by measurements: how can we actually measure whether a conservation law is valid or not, if the very act of measuring a system may change the state (and the energy) of the system? Indeed, measurements are generally disruptive in quantum-mechanical contexts: in a fairly general perspective, measurements are implemented by a collection $\{M_m\}$ of so-called measurement operators [111] that satisfy the completeness relation $\sum_m M_m^\dagger M_m = \mathbb{1}$, with the sub-index m referring to the output of the experiment implemented by the operator M_m; the family $\{E_m\}$ of semi-positive operators defined as $E_m = M_m^\dagger M_m$ is the well-known *Positive Operator-Valued Measure* (POVM). For a given system prepared in a state ρ, the probability of the result m occurring is given by $p_m = \mathrm{Tr}\left(M_m^\dagger M_m \rho\right)$ and the state after the experiment will be

$$\frac{M_m \rho M_m^\dagger}{p_m}. \tag{2.57}$$

The invasive nature of measurement is thus notable, as the state changes from ρ to $(M_m \rho M_m^\dagger)/p_m$ after the measurement.

It may be argued that the conservation laws may still be expected to hold, despite this invasive nature of measurements. However, the content of Wigner-Araki-Yanase (WAY) theorem [74, 75, 79] already provides us evidences that this may not be the case. The theorem (or extensions of it [77]) states that if an observable A is measured and if this measurement is *repeatable*[16], then A must commute with the conserved quantities of the

[15] Using the formalism of Subsection 2.1.1.

[16] This condition can in fact be substituted by Yanase condition, explicitly specified in [77].

system for the conservation laws to hold. Repeatability here means that "*upon immediate repetition of the measurement, the same outcome is achieved with certainty*" (see Eq. 2 of [77]).

Other propositions were intended to further comprehend the role of measurement disturbances and their roles on conservation laws. Gisin and Cruzeiro [109] showed that an seeming violation of the conservation of energy could be solved by including not only the apparatus in the dynamics but also a clock establishing the time of the measurement. A way to suppress the measurement disturbance was considered in [112], where weak measurements were analyzed. In [107, 110], interesting unsolved paradoxes have been introduced leading to apparent violations of the conservation of energy in quantum mechanics; it is not clear yet if such violations actually takes place and from (to) where the quantity is coming (flowing out).

Under a thermodynamics perspective, Elouard et al. [78] proposed that the quantum measurement, seen as a stochastic process, transfers *heat* to the measured system S. Therefore, the apparatus works as a thermal reservoir stochastically modifying its energy. The authors account heat transferred to a system during its measurement as $\mathrm{Tr}(\rho_{\mathrm{S}}(t_+)H_{\mathrm{S}}) - \mathrm{Tr}(\rho_{\mathrm{S}}(t_-)H_{\mathrm{S}})$, where $\rho_{\mathrm{S}}(t_+)$ and $\rho_{\mathrm{S}}(t_-)$ refer to the states before and after the measurement takes place. Although it seems to be a good working hypothesis assuming that the internal energy is $\mathrm{Tr}(\rho_{\mathrm{S}}(t_-)H_{\mathrm{S}})$ before the measurement, it is not generally accepted in quantum mechanics that a property is even well-defined before any measurement, and energy is not an exception. Indeed, if $\rho_{\mathrm{S}}(t_-)$ is a superposition of energies, than the energy is ill-defined before any energy measurement, at least within the standard (Copenhagen) interpretation of quantum mechanics. A way out of this problem, was proposed in [84], where the measured system S and the apparatus A are both included in the dynamical description. In this framework, system and apparatus are weakly measured at an initial time t_1, and subsequently S is measured in terms of a POVM resultant from a unitary coupling with A, followed by a projective measurement of A. They considered a definition of conditional energy, which depends on the result of the projective measurement of the apparatus, so as to account for the variation of energy induced by the measurement. Interestingly, because the system is not strongly measured, the effect of the first measurement is attenuated. However, it can be stated that although weaker, the effect of the first measurement can still change significantly the energy of the whole system, so that one does not describe the "pure" energetic effect of the measurement on the system. Moreover, one may ask whether the notion of conditional energy defined by the authors is a concept extra to the quantum mechanics needed for the description of the transference of energy from the apparatus to the measured system.

Many other routes analyzing measurements and their role on energy balance were presented [76, 82, 83, 86]. Nevertheless, the form of precisely accounting for the energetic effect of a measurement and whether it actually violates conservation laws are still open

matters in the literature.

Though there are evidences that conservation laws do not hold in nontrivial situations, it is generally accepted that conservation laws are *statistically* valid, in the sense that they are averagely satisfied when many copies of the same system are analyzed. Therefore, even though there may be instances and unique protocols in which for a round of an experiment a conservation law is apparently violated, it is still acknowledged that such violations will not occur for many rounds of the same experiment and exact copies of the same system. Nonetheless, even if we accept that conservation laws are valid in terms of distributions and average values, we arrive in another subtler problem: it is not clear how exactly one can *statistically* characterize conservation laws in quantum mechanics, as they invariably involve quantities at different times. For instance, to check whether energy is conserved for a given system from time t_1 to t_2, then one must raise statistics of the variation of energy throughout an interval $[t_1, t_2]$, a task for which quantum mechanics does not have a clear recipe, as we discussed in Subsection 2.5.2. Of course, one can assume the view that, given that the distribution of the energy of a whole system does not evolve in time, then, statistically, the energy should be conserved [25, 98, 110]. But this does not shed light on how to verify the conservation of energy looking at the parts of the system, which is the main strategy used in the literature when analyzing violations. To appreciate this point, we might consider a time-independent hamiltonian operator H analogous to $\mathcal{H}$ in (2.55) and, even though we can verify that the distributions $\langle e_i| \rho |e_i\rangle$ with respect to the eigenvectors $\{|e_i\rangle\}$ of H are unchanged with time, it is not clear whether we can verify an analogous to (2.56) in quantum systems: for that, it is necessary to describe distributions analogous to $\wp_{\mathrm{S,R}}(\Delta, t_1, t_2)$ for two-time quantities, which is not trivially defined in the traditional formalism, as we argued in Section 2.5.2. Indeed, this difficulty has been gaining a great deal of attention in the context of quantum thermodynamics, where quantities such as work, heat, and energy variations and their respective distributions are needed for the thermodynamics description of a given system.

In view of what we discussed throughout this section, we summarize three main unsettling matters, when concerning conservation laws and measurements in the quantum realm: (i) it is not yet clear how to account the energetic disturbance of measurements in quantum mechanics; (ii) it is not certain whether conservation laws can be demonstrated in quantum mechanics and (ii) there is no standard, well-established recipe to compute probability distributions for two-time quantities.

2.8 Elements of reality of two-time quantities

When can a physical quantity be declared well-defined? In a classical context, each variable is assumed to have a unique value at each instant of time, and therefore is well-defined, even before any observer's action and even regardless of the existence of an

observer. Furthermore, even if one cannot access what these unique values are, one can say that they have some defined but unknown value. Therefore, although classical Liouvillian distributions may attribute some subjective or objective (stochastic) ignorance about the variables of a given system, it can be assumed that there are precise values for these that are, however, inaccessible to a given observer.

Now, how about quantum systems? In principle, it seemed that quantum formalism would not describe all variables as well-defined. Indeed, one of the possible interpretations of the Heisenberg uncertainty principle, for example, is that both position and momentum cannot be well-defined for a given preparation. In this sense, it is not that their values are not accessed and they have a precise value; it is just that they do not even have a precise value before any measurement. This quantum feature is quite remarkable and odd when coming from a classical view, and consequently shocked the physics community of the time. Of course, a way out of this conundrum was to investigate whether the quantum theory was incomplete and therefore a more general theory should be considered so that, in this other theory, the variables would be well-defined but for some physically sound reason we cannot access their precise values. The Heisenberg uncertainty, for instance, would therefore be explained from other "more fundamental" principles. In order to categorize a consistent physical theory and verify its completeness, Einstein, Podolsky, and Rosen (EPR) proposed a notion of element of reality [113], which accounts for the notion of a well-defined quantity:

(EPR element of reality) "If, without in any way disturbing a system, we can predict with certainty (i. e. , with probability equal to unity) the value of a physical quantity, then there exists an element of physical reality corresponding to this physical quantity."

This notion together with the assumption that *"every element of reality must have a counterpart"* in a complete theory, led the authors to the conclusion that quantum mechanics is incomplete.

EPR work and its notion of realism rendered, and is still rendering, several investigations and debates (see [114–117] and references therein). Among the criticism against the EPR reality notion is that it does not account for scenarios in which the variables are well-defined, but the observer does not have access to its value for some operational reason, as in the case e.g. of the Liouvillian description. Indeed, a reality notion accounting for these situations was introduced in [114], where Bilobram and Angelo (BA) envisaged a situation in which an observer B can know whether a projective measurement of an observable O_a by other observer A took place. In this scenario, the observer B can assume that O_a is well-defined but he cannot access its exact value, while A can. As a consequence, O_a is an element of the physical reality unknown to B. Encompassing these instances, BA proposed a definition of reality described in a quantum scenario as follows:

"(BA Element of reality). An observable $O_a = \sum_k o_{ak} O_{ak}$, with projectors O_{ak} acting on $\mathbb{H}_a$, is real for a preparation ρ if and only if $\Phi_{O_a}(\rho) = \rho$."

Here, ρ can act on a composite Hilbert space $\mathbb{H} = \mathbb{H}_a \bigotimes_i \mathbb{H}_i$ and the map Φ_{O_a} is defined for the discrete scenario (adaptable for the continuum case [118]) as

$$\Phi_{O_a}(\rho) = \sum_k (O_{ak} \bigotimes_i \mathbb{1}_i)\rho(O_{ak} \bigotimes_i \mathbb{1}_i). \tag{2.58}$$

With this definition in mind, the authors also defined a measure of irreality $\mathcal{I}_{O_a}$, quantifying how far a state is from implying O_a as an element of the physical reality:

$$\mathcal{I}_{O_a}(\rho) = S(\Phi_{O_a}(\rho)) - S(\rho) \equiv S(\rho||\Phi_{O_a}(\rho)) \tag{2.59}$$

where $S(\sigma) = -\operatorname{Tr}(\sigma \ln \sigma)$ is the von Neumann entropy of the state σ and $S(\sigma'||\sigma) = \operatorname{Tr}(\sigma'(\ln \sigma' - \ln \sigma))$ denotes the quantum relative entropy [111]. Interestingly, it can be shown that $S(\Phi_{O_a}(\rho)) \geq S(\rho)$ for any observable O_a, with equality ($\mathcal{I}_{O_a}(\rho) = 0$) if and only if $\Phi_{O_a}(\rho) = \rho$, i.e., the irreality measure is null if and only if O_a is a BA element of reality [114, 117].

Remarkably, $\mathcal{I}_{O_a}(\rho)$ was employed to the analysis of the relation between the reality of an observable of a system S and the flux of information between S and measurement apparatus [117]. Moreover, alternative measures of irreality, in the same spirit as in (2.59), have been investigated in [115]. Recently, $\mathcal{I}_{O_a}(\rho)$ was applied to an experimental investigation of Bohr's complementarity principle [119].

In both EPR and BA definitions of reality, the element of reality is formulated for one-time quantities, such as position, momentum spin, among others. Indeed, it is known that EPR definition can be adapted so as to encompass time as part of it [117, 120]; it is not hard to account time in BA definition as well, by specifying a time t in which the reality is defined and substituting $\rho \to \rho(t)$. A notion of reality for two-time quantities, however, is still elusive.

Certainly, since we are analyzing work in this thesis, we must ask ourselves when work can be understood as a real and well-defined quantity. Of course, this question may be extended to any two-time quantity such as variations of energy, displacements, or even spin variations, for example.

Within the classical paradigm, we implicitly assume that two-time quantities are BA elements of reality, as the trajectories and the properties are well-defined throughout any interval, even if we cannot access them. However, some subtleties cannot be neglected regarding two-time quantities when regarding the EPR element of reality definition, even in a classical context.

Take, for example, the case in which a distribution $\varrho(x, p)$ is attributed to a free particle of mass m, moving in one dimension according to the Hamiltonian $\mathcal{H} = p^2/2m$. Is the displacement of the particle during an interval $[t_1, t_2]$ an EPR element of reality? As we assume general classical Liouvillean distributions, one cannot say so, because one is not a hundred percent sure of $x(t_2) - x(t_1)$. However, if measurements of position x is performed at both instants $t_{1,2}$, then for that round of the experiment, the reality is defined for the displacement. In fact, since one can in principle suppress any disturbance of the

first measurement in the classical context, then the first measurement will only update the information on the position of the particle. However, the first measurement gives no information on the future position, as a full knowledge of the phase point is needed. The second measurement then attest to us which is the second position to which the particle at t_1 goes after a time $t_2 - t_1$. Therefore, as long as we regard position measurements, two measurements are needed so that the displacement in the interval $[t_1, t_2]$ can be taken as an EPR element of reality, and be well-defined in an EPR sense.

However, we can approach the free particle case measuring, instead of the positions at times $t_{1,2}$, the velocity or momentum of the particle at time t_1. In this case, we known that the displacement should be $x(t_2) - x(t_1) = v_1(t_2 - t_1) = \frac{p}{m}(t_2 - t_1)$, even though the positions $x(t_{1,2})$ are unknown. In other words, if a measurement of velocity or momentum is made at time t_1 then the displacement during $[t_1, t_2]$ can be said to be EPR real, even if the positions at $t_{1,2}$ are not. Therefore, only an initial measurement is needed to define an element of reality for the displacement.

Of course this discussion on displacement can be extended for more general classical scenarios, accounting also for other quantities such as work or variation of energy. Invariably, the general conclusion is that one can specify an EPR element of reality for a two-time quantity by measuring a sufficient number of initial variables; alternatively, one can measure two-time quantities in both times and the same result on both approaches are expected to be valid in the classical case.

We may as well ask ourselves what would happen in a quantum scenario: in the example of the free particle, should both categories of measurements (two-time position or velocity) give the same result? How can we state, in the quantum world, whether a displacement or other two-time quantity is well-defined, and is therefore an element of reality? In the following chapter, we propose an answer to these questions.

2.9 Take-away messages and goals

We presented in this chapter some perspectives of work in the classical and quantum scenarios. In a classical context, we approached the mechanical, thermodynamic, physical-statistical and thermodynamic-stochastic definitions of work. We noticed that the unambiguous and general mechanical definition of work allows the natural emergence of the concept of internal energy, so that the work-energy principle could be established. Furthermore, it is expected that, through the Liouvillian formalism of classical distributions, the mechanical definition and the Work-Energy principle are still consistent.

We discussed the subtle differences between the concept of work coming from mechanics and thermodynamics. Moreover, we exposed the fact that, if the definitions used in stochastic thermodynamics are considered for general microscopic cases, then some obstacles regarding the definition of internal energy may arise. Also, we showed scenarios

in which the definition of heat can have a form similar to the definition of work from statistical physics, an apparent inconsistency.

We reviewed approaches in the quantum scenario where the thermodynamic notions of work are problematic when regarding general states and small systems. Additionally, the difficulty of raising statistics and measuring work were shown to be an open matter in the literature.

We pointed out that the measurement-induced disturbance in the quantum context is still an open subject and enunciated main problems in this direction. In the end, we reported that the very concept of reality of two-time quantities, of which work is an example, was not yet proposed in the literature.

In summary, we raised the following questions:

- How to define internal energy in the quantum context?
- Is it possible to construct a quantum-mechanical definition of work for general systems and states in an autonomous dynamics?
- Can one associate a quantum observable to the notion of work? How to measure work and other two-time quantities and raise their statistics?
- Is it possible to construct a definition of "useful" work as a form of energy transfer associated with a trackable semi-classical variable for autonomous systems?
- How to evaluate the energetic disturbance induced by measurements in quantum mechanics?
- Can conservation laws be demonstrated in quantum mechanics?
- When can work and other two-time quantities be declared well-defined or an element of the physical reality?

Our objective in this thesis is to propose answers to these questions, so as to be able to construct a more precise conceptual framework for the law of conservation of energy in quantum mechanics. To achieve this goal we use a "bottom-up" strategy.

First, we propose a quantum mechanical (QM) definition of work that satisfies the principle and criteria described in Section 2.1. We guarantee, by construction, that our definition induces a clear notion of internal energy and establishes its relation to external work. We also show that work can be seen as a quantum observable and analyze its statistics and measurements.

Equipped with the QM work and its underlying notion of internal energy, we then propose a form of describing the role of measurement. In this context, we demonstrate a general limit on the energetic disturbance imposed by the measurement. Moreover, we discuss how the conservation law can still be valid in a measurement scenario.

In Chapter 5, we show some general features and explore some bounds on QM work, in the spirit of Section 2.6.

In the second part of the thesis, we explore situations in which thermodynamics and mechanics intersects. We derive some quantum mechanical work fluctuation relations, in which the state of the system is non-trivial.

We then examine how a definition of work with a form close to the physical-statistical perspective can emerge from our purely mechanical description, even in autonomous scenarios. This work is constructed in a way such as to be closely related to variables similar to the NFVs presented in Subsection 2.5.3 and, by construction, allows one to overcome the obstacles mentioned there. Furthermore, we show that this form of work converges to the HB definition for special cases.

3 Quantum mechanical work

Here we introduce our approach on quantum mechanical (QM) work, a concept crucial to the bottom-up structure of this thesis. Our attitude consists of closely following the classical structure of Section 2.1, and is similar to what we have done in our article [121], published in *Physical Review A* during the doctoral period, which was partly inspired by the masters dissertation in [122].

3.1 QM work: the definition

An important obstacle to suit a mechanical notion of work to the quantum domain might be the absence of direct notions of velocity and force in the quantum domain. However, as we show next, this can be remedied with use of the Heisenberg picture, wherein the operators are written as $O \equiv O(t) \equiv \phi_t(O^{\mathfrak{s}})$, where $O^{\mathfrak{s}}$ is the corresponding Schrödinger operator[1] and ϕ_t is the time-evolution map satisfying $\phi_t^* = \phi_{-t}$ and $\phi_{t_1}\phi_{t_2} = \phi_{t_1+t_2}$. In particular, for unitary evolutions respecting $i\hbar\,\dot{U}_t = HU_t$, one has $\phi_t^*(\rho_0) = U_t\,\rho_0\,U_t^\dagger$ and $O = \phi_t(O^{\mathfrak{s}}) = U_t^\dagger\,O^{\mathfrak{s}}\,U_t$. Let us consider a universe $\mathrm{U} = \{1, 2, \cdots, N\}$ composed of N spinless interacting particles whose dynamics is described by the Hamiltonian operator

$$H = \sum_{i=1}^{N} \frac{P_i^2}{2m_i} + \sum_{j>i=1}^{N} V_{ij}, \tag{3.1}$$

where $V_{ij} = V_{ij}(|X_i - X_j|)$. In Heisenberg's picture, the velocity operator and the resultant force operator for the i-th particle are respectively written as $\dot{X}_i = [X_i, H]/i\hbar$ and $m_i\ddot{X}_i = m_i[\dot{X}_i, H]/i\hbar$. The quantum state ρ_0 and the Hamiltonian H act on a joint Hilbert space $\mathbb{H}_\mathrm{U} = \bigotimes_{k=1}^{N} \mathbb{H}_k$, whereas X_i and P_i act on $\mathbb{H}_i$. We then introduce our candidate for the *resultant quantum mechanical work* done on particle i:

$$W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1) = \tfrac{1}{2}\int_{t_1}^{t_2} dt\; m_i\{\dot{X}_i, \ddot{X}_i\}, \tag{3.2}$$

where, using the notation of the previous chapter, our system of interest is described by $\mathrm{S} = \{i\}$ and the environment is $\mathrm{E} = \mathrm{U} - \mathrm{S}$. The symmetrization $\frac{1}{2}\{A, B\} = \frac{1}{2}(AB + BA)$ aims at ensuring Hermiticity. It should be recognized from the very beginning that $W_{\mathrm{E}\to\mathrm{S}}$ is an operator acting on the joint Hilbert space $\mathbb{H}_\mathrm{U} = \mathbb{H}_\mathrm{S} \otimes \mathbb{H}_\mathrm{E}$, the consequences of which will be discussed posteriorly.

Now, one can show by direct integration of the Heisenberg equation $d\dot{X}_i^2/dt = [\dot{X}_i^2, H]/i\hbar = \{\dot{X}_i, \ddot{X}_i\}$ that

$$\frac{m_i\dot{X}_i^2(t_2)}{2} - \frac{m_i\dot{X}_i^2(t_1)}{2} = \frac{1}{2}\int_{t_1}^{t_2} dt\; m_i\{\dot{X}_i, \ddot{X}_i\}, \tag{3.3}$$

[1] The superscript $\mathfrak{s}$ will be used hereafter to denote operators in the Schrödinger picture.

which is the algebraic statement of the energy-work theorem $\Delta E_{\mathrm{S}} = W_{\mathrm{E}\to\mathrm{S}}$ with respect to the internal energy operator $E_{\mathrm{S}} \equiv K_i(t) = m_i \dot{X}_i^2(t)/2 = P_i^2/2m_i$. Also, just as in the classical context, this approach allows us to speak of the notion of "work done by a force". Plugging the Heisenberg equation $m_i \ddot{X}_i = \dot{P}_i = -\sum_{j\in\mathrm{E}} \partial_{X_i} V_{ij}$ into (3.2) induces us to introduce

$$W_{j\to i}(t_2, t_1) = -\frac{1}{2}\int_{t_1}^{t_2} dt\, \{\dot{X}_i, \partial_{X_i} V_{ij}\}, \tag{3.4}$$

which makes direct reference to its classical counterpart (see Section 2.1). This means that whenever one is able to identify a specific physical potential in the system under consideration, then the recipe (3.4) can be used to describe the work mediated by the interaction V_{ij} in the time interval $[t_1, t_2]$. The sum of all individual contributions yields the resultant quantum mechanical work, $W_{\mathrm{E}\to\mathrm{S}} = \sum_{j\in\mathrm{E}} W_{j\to i}$, which causes the change in the internal energy, as prescribed by (3.3).

We can extend our analysis so as to describe a system of interest with more than one particle, as in the classical context. Setting $\mathrm{S} = \{1, 2, \cdots, M\}$ and $\mathrm{E} = \{M+1, M+2, \cdots, N\}$ one shows via some algebra that

$$W_{\mathrm{E}\to\mathrm{S}} = \sum_{j\in\mathrm{E}}\sum_{i\in\mathrm{S}} W_{j\to i} = \Delta\left(\sum_{i=1}^{M} K_i + \sum_{k>i=1}^{M} V_{ik}\right) \equiv \Delta E_{\mathrm{S}}. \tag{3.5}$$

This is the exact quantum counterpart of (2.5) via calculations similar to those employed around (2.4) in Section 2.1. Hence, in perfect analogy with the classical framework, the definition of the total work imparted on the system S reveals the internal-energy operator $E_{\mathrm{S}} = H_{\mathrm{S}}$ without any ambiguity. In particular, it is notorious that the Schrödinger version $E_{\mathrm{S}}^{\mathrm{s}} = H_{\mathrm{S}}^{\mathrm{s}} \otimes \mathbb{1}_{\mathrm{E}}$ of this operator effectively acts on $\mathbb{H}_{\mathrm{S}}$ only, and so does E_{S} when one "turns off" the interaction with the environment. That is, the coupling between S and E does not count as internal energy. The theoretical strategy used in the classical context of "turning off" the environment allows us to identify what the internal energy should be in our formalism, thus avoiding the inclusive-versus-exclusive ambiguity.

It is opportune to remark that our approach can be straightforwardly extended to more than one dimension, thus being able to implement the principle of conservation of energy, $\Delta E_{\mathrm{S}} = W_{\mathrm{E}\to\mathrm{S}}$, in general mechanical contexts. In scenarios involving electromagnetic phenomena, if one can unambiguously identify the internal energy operator E_{S} (for example, by "turning off" all interactions with the environment), then one can take (3.5) as a fundamental postulate, from which the work done on S by E can be computed as ΔE_{S}. For instance, if the internal energy is represented by some Hamiltonian operator $H_{\mathrm{S}}^{\mathrm{s}} \in \mathbb{H}_{\mathrm{S}}$, then the relation

$$W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1) = \phi_{t_2}\left(H_{\mathrm{S}}^{\mathrm{s}} \otimes \mathbb{1}_{\mathrm{E}}\right) - \phi_{t_1}\left(H_{\mathrm{S}}^{\mathrm{s}} \otimes \mathbb{1}_{\mathrm{E}}\right) \tag{3.6}$$

gives the work operator done on S by E in the time interval $[t_1, t_2]$. Therefore, we can restate the Work-Energy principle, in a quantum scenario:

Principle 2. ***(Quantum Work-Energy)*** *Work done on a given system of interest* S *is equal the change in its internal energy operator, as described in* (3.6).

Generic expectation values of work are therefore computed as $\langle g(W_{\mathrm{E}\to\mathrm{S}})\rangle\,(t_2,t_1) = \mathrm{Tr}[g(W_{\mathrm{E}\to\mathrm{S}})\rho_0]$, for well behaved functions g. In particular, the mean work and its uncertainty follow from

$$\langle W_{\mathrm{E}\to\mathrm{S}}\rangle = \mathrm{Tr}\left(W_{\mathrm{E}\to\mathrm{S}}\,\rho_0\right), \tag{3.7a}$$

$$\sigma_{W_{\mathrm{E}\to\mathrm{S}}} = \left(\langle W^2_{\mathrm{E}\to S}\rangle - \langle W_{\mathrm{E}\to S}\rangle^2\right)^{1/2}, \tag{3.7b}$$

with analogous relations for the work imparted by a specific force [Eq. (3.4)]. In fact, if the interaction V_{AB} between a system A and B is well-defined, based on fundamental physical principles, then it is reasonable to compute the work done exclusively by B on A as

$$W_{\mathrm{B}\to\mathrm{A}} = \int_{t_1}^{t_2} dt\,\frac{[H_{\mathrm{A}}(t), V_{\mathrm{AB}}(t)]}{i\hbar}. \tag{3.8}$$

In fact, this form follows directly from the work definition in the case of the particle scenario described in (3.1).

3.2 Work as an observable

As we exposed in Subsection 2.5.2, an intense debate regarding the assignment of a quantum observable to work was conducted in the literature. As we reviewed, several of the criticisms were done against the idea of work as an observable essentially because it does not restore the classical fluctuation relations. We argued, in accordance with [63], that despite the demonstrated relevance of the results of classical stochastic thermodynamics, they are not expected to be valid in general quantum contexts, so that a work operator should not be automatically discarded for not leading to them. Although all this debate was conducted exclusively within the framework of the (quantum and classical) stochastic thermodynamics, our approach here, assuming a mechanical perspective of work instead of a thermodynamics one, may not necessarily be immune to the aforementioned objections. In what follows, we discuss some emblematic physical problems through which we demonstrate the adequacy of assuming work as well as other two-time quantities as a quantum observable, so as to preserve the quantum mechanics axiom according to which *every* physical quantity is to be described within the quantum formalism as an observable.

3.2.1 Work due to a uniform gravitational field

We start with the simple instance in which a particle S of mass m is immersed in a homogeneous gravitational field g created by a massive body E (the Earth), which remains

fixed at the origin of the inertial coordinate system. This turns out to effectively be a one-body model described by

$$H = \frac{P^2}{2m} + mgX, \tag{3.9}$$

where X (P) stands for the position (momentum) operator. We believe that nobody would object to the idea that E does some work on S, and yet, since there is no external driving $\lambda(t)$, prescription (1.4) yields $\partial_\lambda(P^2/2m) = 0$ and $\mathcal{W}(t_2, t_1) = 0$. To apply our formalism, we first compute the Heisenberg equations $\dot{X} = P/m$ and $\dot{P} = -mg = m\ddot{X}$, and then we find the solutions $P(t) = P^{\mathrm{s}} - mgt = m\dot{X}$ and $X(t) = X^{\mathrm{s}} + P^{\mathrm{s}}t/m - gt^2/2$. Using (3.2) and (3.3), we obtain the work operator

$$W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1) = \Delta E_{\mathrm{S}} = -g\,(t_2 - t_1)\; P^{\mathrm{s}} + \tfrac{mg^2}{2}\left(t_2^2 - t_1^2\right), \tag{3.10}$$

where $E_{\mathrm{S}} = K = m\dot{X}^2/2$. Clearly, the potential $V = mgX$ is not part of the internal energy of S. Since the operators of the (classical) heavy particle E do not enter the model, then $\frac{1}{2}dt\{\dot{X}, \partial_X V\} = \dot{V}dt$. It follows from (3.4) that

$$W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1) = -\Delta V = mg\left[X(t_1) - X(t_2)\right]. \tag{3.11}$$

Not surprisingly, Eqs. (3.10) and (3.11) give $\Delta(K + V) = \Delta H = 0$. It is clear from the above results that the work operator has the same right as P^{s} to be understood as an observable. In particular, it is Hermitian and satisfies the relation

$$W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1)\,|p\rangle = w_p(t_2, t_1)\,|p\rangle\,, \tag{3.12}$$

with eigenvalues $w_p(t_2, t_1) = -g(t_2 - t_1)p + mg^2\left(t_2^2 - t_1^2\right)/2$ and eigenvectors $|p\rangle$ such that $P^{\mathrm{s}}|p\rangle = p\,|p\rangle$.

As an interesting consequence of Eq. (3.12), by measuring the momentum of the particle and thus preparing, say, $\rho_0 = |p_0\rangle\langle p_0|$ as an initial state, one automatically prepares the amount $w_{p_0}(t_2, t_1)$ of work that E will impart on S in the time interval $[t_1, t_2]$. Since the initial state is a work eigenstate, one has a scenario in which there is no uncertainty whatsoever for the observable work. Also, it follows that $\langle W_{\mathrm{E}\to\mathrm{S}}\rangle = w_p(t_2, t_1)$, which coincides with the value expected from classical mechanics. For instance, we have $w_{p_0}(t, 0) = \mathrm{f}_g\,\Delta x(t)$, where $\mathrm{f}_g = -mg$ and $\Delta x(t) = p_0 t/m - gt^2/2$. This is in full agreement with the Ehrenfest theorem [123, 124]. Remarkably, through a single measurement, one is able to set the amount of work that will be executed in an arbitrary time interval. This is not to say, though, that work is a (time local) state variable. In fact, by construction, the work observable is a two-time operator satisfying $W_{\mathrm{E}\to\mathrm{S}}(t, t) = 0$. In addition, it is clear that the resulting eigenvalue makes reference to a classical trajectory whose segment $x(t_2) - x(t_1)$ characterizes the process through which E changes S's internal energy.

To avoid issues concerning the normalization of the quantum state, one can always associate $\rho_0 = |p_0\rangle\langle p_0|$ with a very sharp Gaussian state or think of it as the projection $\rho_0 = \int_{p_0 - d_p/2}^{p_0 + d_p/2} dp\;|p\rangle\langle p| \cong |p_0\rangle\langle p_0|\,d_p$, with d_p being the resolution for momentum

measurements. Alternatively, we can use methods that treat momentum as a discrete variable [118]. In any of these cases, however, from a physical point of view, we do expect some superposition of momentum eigenvectors, which naturally implies a superposition of work, with an associated mean value and quantum uncertainty.

3.2.2 Work due to an elastic potential

Now we conceive a universe $\mathrm{U} = \{1,2\}$ with two particles of masses $m_{1,2}$ interacting via an elastic potential of characteristic constant k. The unitary autonomous dynamics is governed by the Hamiltonian

$$H = \frac{P_1^2}{2m_1} + \frac{P_2^2}{2m_2} + \frac{k}{2}(X_2 - X_1)^2, \tag{3.13}$$

where X_i (P_i) is the position (momentum) operator of the i-th particle. Here we set $\mathrm{S} = 1$ and $\mathrm{E} = 2$. By means of the usual transformation

$$\begin{aligned} X_{\mathrm{cm}} &= \frac{m_1 X_1 + m_2 X_2}{M}, & X_{\mathrm{r}} &= X_2 - X_1, \\ P_{\mathrm{cm}} &= P_1 + P_2, & P_{\mathrm{r}} &= \mu\left(\frac{P_2}{m_2} - \frac{P_1}{m_1}\right), \end{aligned} \tag{3.14}$$

with $\mu = m_1 m_2 / M$ and $M = m_1 + m_2$, we can rewrite the Hamiltonian in the form $H = P_{\mathrm{cm}}^2/2M + P_{\mathrm{r}}^2/2\mu + kX_{\mathrm{r}}^2/2$, which shows that the center-of-mass part decouples from the relative one. As a consequence, one can write the time-evolution operator as $U_t = U_{\mathrm{cm}} \otimes U_{\mathrm{r}}$, which then yields the solutions

$$\begin{aligned} X_{\mathrm{cm}} &= X_{\mathrm{cm}}^{\mathrm{s}} + \tfrac{P_{\mathrm{cm}}^{\mathrm{s}} t}{M}, & X_{\mathrm{r}} &= X_{\mathrm{r}}^{\mathrm{s}} \cos(\omega t) + \tfrac{P_{\mathrm{r}}^{\mathrm{s}}}{\mu\omega} \sin(\omega t), \\ P_{\mathrm{cm}} &= P_{\mathrm{cm}}^{\mathrm{s}}, & P_{\mathrm{r}} &= P_{\mathrm{r}}^{\mathrm{s}} \cos(\omega t) - \mu\omega X_{\mathrm{r}}^{\mathrm{s}} \sin(\omega t), \end{aligned} \tag{3.15}$$

with $\omega = \sqrt{k/\mu}$. Returning to the original variables, we can write the work observable as $W_{\mathrm{E}\to\mathrm{S}}(t_2,t_1) = K_1(t_2) - K_1(t_1)$, where $K_1 = P_1^2/2m_1$ and

$$P_1(t) = a(t)\, P_1^{\mathrm{s}} + b(t)\, P_2^{\mathrm{s}} + c(t)\,(X_2^{\mathrm{s}} - X_1^{\mathrm{s}}), \tag{3.16}$$

$$\begin{aligned} a(t) &= [m_1 + m_2 \cos(\omega t)]\,/M, \\ b(t) &= [1 - \cos(\omega t)]\, m_1/M, \\ c(t) &= \mu\omega \sin(\omega t). \end{aligned} \tag{3.17}$$

Although an explicit form of the work operator can be easily derived from the above formulas, it is not insightful and its diagonalization is not trivially feasible. We then restrict our analysis to convenient instants of time. An instructive example is

$$W_{\mathrm{E}\to\mathrm{S}}(v\tau, u\tau) = 2\left[\tfrac{m_1 - m_2}{M^2} P_1^{\mathrm{s}} P_2^{\mathrm{s}} + \tfrac{m_1}{M^2}(P_2^{\mathrm{s}})^2 - \tfrac{m_2}{M^2}(P_1^{\mathrm{s}})^2\right], \tag{3.18}$$

with $\tau = \pi/\omega$, v (u) an odd (even) integer, and $v > u \geq 0$. Here, $P_1^{\mathrm{s}} P_2^{\mathrm{s}}$ is used as a shorthand for $P_1^{\mathrm{s}} \otimes P_2^{\mathrm{s}}$. The work operator is diagonal in the composite basis $\{|p_1\rangle\,|p_2\rangle\}$, where $P_i^{\mathrm{s}}\,|p_i\rangle = p_i\,|p_i\rangle$, and its eigenvalues read

$$w_{p_1,p_2}\left(v\tau, u\tau\right) = 2\left(\tfrac{m_1-m_2}{M^2} p_1 p_2 + \tfrac{m_1}{M^2} p_2^2 - \tfrac{m_2}{M^2} p_1^2\right). \tag{3.19}$$

Hence, by measuring $P_{1,2}^{\mathrm{s}}$ one prepares the amount w_{p_1,p_2} of work in the time interval $[u\tau, v\tau]$. Notice, however, that this is a joint measurement, that is, both particles have to be touched. This example offers a better picture of the typical work operator: it is an observable acting on a composite vector space and quantum theory allows, in these cases, the existence of entangled work eigenstates. To see this, consider the initial state $|\psi_0\rangle = |\bar{p}_1\rangle\,|\bar{p}_2\rangle$, where $|\bar{p}_{1,2}\rangle$ are sharp Gaussian states centered at $\bar{p}_{1,2}$, thus ensuring a well defined mean work. Now, in terms of the relative and center-of-mass momentum, the work operator (3.18) reads $W_{\mathrm{E}\to\mathrm{S}}\left(v\tau, u\tau\right) = \frac{2}{M} P_{\mathrm{cm}}^{\mathrm{s}} P_{\mathrm{r}}^{\mathrm{s}}$. This change of variables implies that

$$\frac{e^{-\frac{(p_1-\bar{p}_1)^2}{4\delta_p^2}}}{(2\pi\delta_p^2)^{1/4}} \frac{e^{-\frac{(p_2-\bar{p}_2)^2}{4\delta_p^2}}}{(2\pi\delta_p^2)^{1/4}} = \frac{e^{-\frac{(p_{\mathrm{r}}-\bar{p}_{\mathrm{r}})^2}{4\delta_{\mathrm{r}}^2}}}{(2\pi\delta_p^2)^{1/4}} \frac{e^{-\frac{(p_{\mathrm{cm}}-\bar{p}_{\mathrm{cm}})^2}{4\delta_{\mathrm{cm}}^2}}}{(2\pi\delta_p^2)^{1/4}} e^{-\frac{\alpha p_{\mathrm{r}} p_{\mathrm{cm}} + \beta}{\delta_p^2}}, \tag{3.20}$$

where $\bar{p}_{\mathrm{r}}$, $\bar{p}_{\mathrm{cm}}$, δ_{r}, δ_{cm}, α, and β are functions of the width δ_p and $\bar{p}_{1,2}$. From $\alpha = \frac{1}{2}\frac{m_2-m_1}{m_1+m_2}$, we see that the initial state is entangled in the new degrees of freedom whenever $m_2 \neq m_1$. Conversely, preparing a product state $|\bar{p}_{\mathrm{r}}\rangle\,|\bar{p}_{\mathrm{cm}}\rangle$ for these "nonlocal degrees of freedom" renders an entangled state in $p_{1,2}$.

Recognizing that work is an observable allows one to envisage interesting scenarios whereby Alice can steer the work done in Bob's laboratory. Consider an instance in which an ancillary system A is prepared, along with particles 1 and 2, in the state $|\Psi\rangle = \alpha\,|a\rangle\,|w_{p_1,p_2}\rangle + \beta\,|\bar{a}\rangle\,|w_{\bar{p}_1,\bar{p}_2}\rangle$, where $|w_{p_1,p_2}\rangle \equiv |p_1\rangle\,|p_2\rangle$ and $\langle a|\bar{a}\rangle = 0$, as depicted in Fig. 3.1.

Let us assume that the state $|\Psi\rangle$ can be preserved while the ancilla is transported to Alice's laboratory, which is far away from Bob's site where particles 1 and 2 are allowed to interact with each other according to the Hamiltonian (3.13). For generic amplitudes α and β, the state $|\Psi\rangle$ is entangled and possesses other subtle quantum correlations, such as Einstein-Podolsky-Rosen (EPR) steering [125] and Bell nonlocality [126]. This does not imply that Alice can effectively control the average amount of work that will take place in Bob's laboratory, for her measurement outcomes are random. The presence of EPR steering means that one cannot ascertain, before any measurement, an element of reality for work. That is, referring back to Eq. (3.19), the amount of work that particle 2 will do on particle 1 in the time interval $[u\tau, v\tau]$ cannot be ensured by any local hidden variable theory to be either w_{p_1,p_2} or $w_{\bar{p}_1,\bar{p}_2}$. Only after Alice measures the ancilla in her far distant laboratory, thus collapsing the system state to either $|a\rangle\,|w_{p_1,p_2}\rangle$ or $|\bar{a}\rangle\,|w_{\bar{p}_1,\bar{p}_2}\rangle$, will the amount of work in Bob's laboratory materialize to either w_{p_1,p_2} or $w_{\bar{p}_1,\bar{p}_2}$, respectively. What is more, such

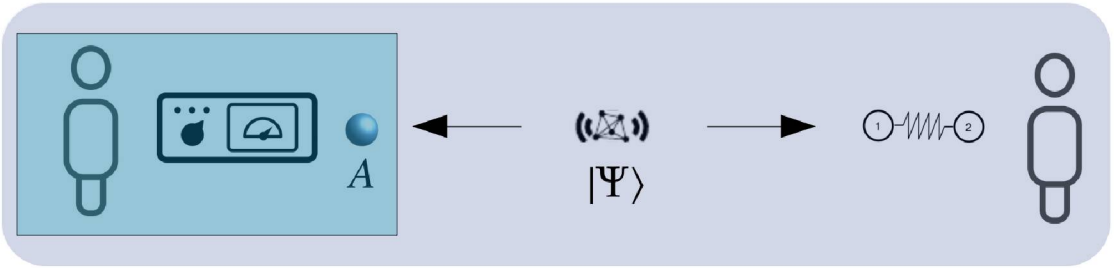


Figure 3.1 – A source prepares a state $|\Psi\rangle = \alpha\,|a\rangle\,|w_{p_1,p_2}\rangle + \beta\,|\bar{a}\rangle\,|w_{\bar{p}_1,\bar{p}_2}\rangle$ where the ancillary system A, related to the eigenvectors $|\bar{a}\rangle\,, |a\rangle$, is sent to Alice's lab on the left, while the two-particle system, with work eigenstates $|w_{p_1,p_2}\rangle\,, |w_{\bar{p}_1,\bar{p}_2}\rangle$, is sent to Bob, on the right. Alice can steer work on Bob's location, by measuring the ancillary system any instant after the state preparation at $t = 0$ prior to the time interval $[u\tau, v\tau]$, with $\tau = \pi/\omega$, v (u) an odd (even) integer, and $v > u \geq 0$. Before her measurement, work done by particle 2 on 1 is not defined (it is in a quantum superposition). On the other hand, it is only after her measurement that the amount of work on the far distant Bob's location will have a well-defined value for the intervals $[u\tau, v\tau]$ ($t \leq u\tau$), either collapsing to w_{p_1,p_2} or $w_{\bar{p}_1,\bar{p}_2}$.

nonlocal work steering can be implemented by Alice's measurement at any instant after the state preparation at $t = 0$ and prior to the time interval $[u\tau, v\tau]$.

It is worth noticing that one does not really *measure* a two-time observable, like work or displacement, at a given instant of time t after the preparation. In fact, this cannot be done even within the classical paradigm simply because a two-time observable is not definable at a single time. Instead, we *prepare* it for the time interval $[t_1, t_2]$ through the establishment of ρ_0 at $t = 0$. As we shall discuss later, work should accordingly be viewed as a two-time element of reality.

3.2.3 Work statistics

Once work is treated as an observable, one can determine its eigenstates, the corresponding projectors, and the emergent probability distributions. In other words, one can raise the entire statistics associated with its preparation. As we thoroughly described in Subsection 2.5.2, an alternative view that has commonly been adopted, especially in contexts involving an external driving parameter $\lambda(t)$, conceives work as a stochastic variable that can only be inferred through a TPM protocol, i.e. two projective measurements of energy for the same round of the experiment. In this section, we confront these two views emphasizing their conflicting results. As we reviewed, the application of the TPM protocol to thermodynamic contexts typically presumes (i) a nonautonomous dynamics wherein $H_{\rm S}^{\rm s}(t) = H_{\rm S}^{\rm s}\left(\lambda(t)\right)$, (ii) the coupling with this device as part of the internal energy [97], and (iii) initial states such that $[\rho_{\rm S}(0), H_{\rm S}^{\rm s}(0)] = 0$. Since these conditions are not met in the mechanical context under scrutiny here, some adaptations in the protocol will be in order.

Now, to appreciate the differences among the approaches, we focus on the problem of free fall, as treated in Section 3.2.1. The corresponding classical model encompasses the

Hamiltonian function $\mathcal{H} = p^2/2m + mgx$, which yields the work $\mathcal{W}_{\mathrm{E}\to\mathrm{S}} = \Delta\mathcal{K} = -\Delta\mathcal{V}$, where $\mathcal{K} = p^2/2m$ and $\mathcal{V} = mgx$. This double identity, which also emerges in our approach to quantum work, induces one to conceive two variations of the typical TPM protocol, one for measurements of momentum (and thus kinetic energy) and another involving measurements of position (potential energy). Accordingly, we refer to these protocols as TPM_p and TPM_x respectively, depicted in Fig. 3.2.

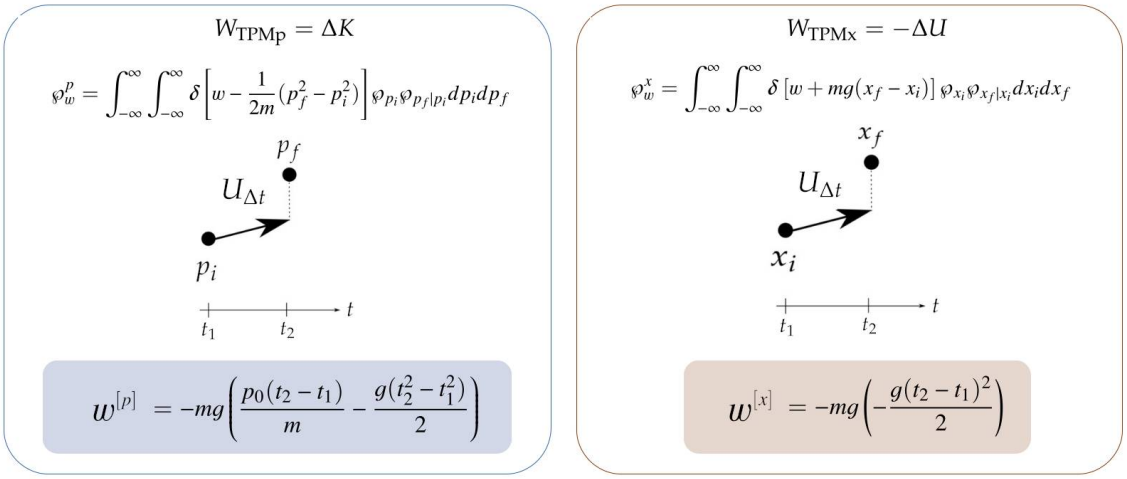


Figure 3.2 – Schematic representation of two possible TPM statistical descriptions of work in the gravitational case. In a TPM_p scheme (left), work equals the variation of kinetic energy and the TPM scheme is implemented by measuring momentum at times $t_{1,2}$, so that the kinetic energy variation in the interval $[t_1, t_2]$ as well as TPM work statistics $\wp_w^p(t_2, t_1)$ can be computed. On the other hand, in a TPM_x procedure (right), the position, and, therefore, the potential energies are measured at the same times $t_{1,2}$, so that work can be taken as the negative of the variation of the potential energy and its statistics $\wp_w^x(t_2, t_1)$ can be computed. It turns out that the two TPM protocols do not agree about (i) the mean work done on the particle and (ii) the work statistics, therefore failing to demonstrate the conservation of energy for this simple model, even for semi-classical scenarios.

In both cases, the preparation will be a Gaussian pure state $\rho_0 = |\psi_0\rangle\langle\psi_0|$ with corresponding wave function

$$\psi_0(x) = \langle x|\psi_0\rangle = \left(2\pi\sigma_x^2\right)^{-\frac{1}{4}} \exp\left[-\frac{(x-x_0)^2}{4\sigma_x^2} + \frac{ip_0x}{\hbar}\right], \tag{3.21}$$

where $\langle X^{\mathrm{s}}\rangle = x_0$, $\langle P^{\mathrm{s}}\rangle = p_0$, and $\sqrt{\langle (X_*^{\mathrm{s}})^2\rangle} = \sigma_x$ with $X_*^{\mathrm{s}} \equiv X^{\mathrm{s}} - \langle X^{\mathrm{s}}\rangle$. For notation compactness, we use $\mathcal{G}_u(\bar{u}, \sigma) = (2\pi\sigma^2)^{-\frac{1}{2}} \exp\left[-\frac{(u-\bar{u})^2}{2\sigma^2}\right]$ for Gaussian functions with width σ and center at $\bar{u}$. The next step consists of unitarily evolving the initial state from $t = 0$ until $t = t_1$, then performing the first measurement. Regarding a similar procedure as in [127], we can describe the time-evolution operator until the first measurement at time t_1 as[2]

$$U_{t_1} = e^{-i\Theta t_1} \exp\left(-\frac{imgt_1X}{\hbar}\right) \exp\left(-\frac{iP^2t_1}{2m\hbar}\right) \exp\left(\frac{igt_1^2P}{2\hbar}\right), \tag{3.22}$$

[2] To obtain the factorized form (3.22), we first move the description to the interaction picture via the transformation $|\overline{\psi}\rangle = e^{imgXt/\hbar}|\psi\rangle$. The time-evolution operator for the new Schrödinger equation, $i\hbar\,\partial_t|\overline{\psi}\rangle = \frac{(P-mgt\mathbb{1})^2}{2m}|\overline{\psi}\rangle$, can be directly factorized as $e^{-iP^2t/2m\hbar}e^{igt^2P/2\hbar}$.

where $\Theta_{t_1} = \frac{mg^2t_1^3}{6\hbar}$. The probability densities associated with the outcomes r_i in the first measurements of $r \in \{x, p\}$ at t_1 read

$$\begin{aligned} \wp_{x_i} &= |\langle x_i|\psi(t_1)\rangle|^2 = \mathcal{G}_{x_i}\left(x_0 + \tfrac{p_0 t_1}{m} - \tfrac{gt_1^2}{2}, \sigma_x(t_1)\right), \\ \wp_{p_i} &= |\langle p_i|\psi(t_1)\rangle|^2 = \mathcal{G}_{p_i}\left(p_0 - mgt_1, \tfrac{\hbar}{2\sigma_x}\right), \end{aligned} \tag{3.23}$$

where $\sigma_x(t_1) = \sigma_x\sqrt{1 + (\hbar t_1/2m\sigma_x^2)^2}$. We assume that after a position (momentum) measurement the state is a Gaussian one with width d_x (d_p) referring to the measurement resolution (which are eventually taken to be ideal, that is, $d_r \to 0$). Therefore, the state reduces to the eigenstate $|r_i\rangle$, here expressed as $\langle r|r_i\rangle = \sqrt{\mathcal{G}_r(r_i, d_r)}$. Then, we apply the evolution operator (3.22) with the change $t_1 \to \Delta t = t_2 - t_1$ and compute the conditional probability densities needed for the TPM procedure

$$\begin{aligned} \wp_{x_f|x_i} &= \left|\langle x_f|U_{\Delta t}|x_i\rangle\right|^2 = \mathcal{G}_{x_f}\left(x_i - \tfrac{g\Delta t^2}{2}, d_x(\Delta t)\right), \\ \wp_{p_f|p_i} &= \left|\langle p_f|U_{\Delta t}|p_i\rangle\right|^2 = \mathcal{G}_{p_f}\left(p_i - mg\Delta t, d_p\right), \end{aligned} \tag{3.24}$$

where $d_x(\Delta t) = d_x\sqrt{1 + (\hbar\Delta t/2md_x^2)^2}$. Taking $e_{i,f}^{[x]} = mgx_{f,i}$ and $e_{i,f}^{[p]} = p_{i,f}^2/2m$ for the TPM_x and TPM_p protocols, respectively, we can compute work distributions as $\wp_w^{[r]}(t_2, t_1) = \iint dr_i dr_f\, \wp_{r_i}\wp_{r_f|r_i}\delta_{\mathrm{D}}\left[w - (e_f^{[r]} - e_i^{[r]})\right]$. The results read

$$\wp_w^{[r]}(t_2, t_1) = \mathcal{G}_w\left(w^{[r]}(t_2, t_1), \sigma_w^{[r]}\right), \tag{3.25}$$

where $w^{[r]}(t_2, t_1) = \mathrm{f}_g\Delta_x^{[r]}$ (mean work), $\mathrm{f}_g = -mg$, and

$$\begin{aligned} \Delta_x^{[x]} &= -\tfrac{g\Delta t^2}{2}, & \sigma_w^{[x]} &= |\mathrm{f}_g|d_x(\Delta t), \\ \Delta_x^{[p]} &= \tfrac{p_0\Delta t}{m} - \tfrac{g(t_2^2 - t_1^2)}{2}, & \sigma_w^{[p]} &= \sigma_p g\Delta t. \end{aligned} \tag{3.26}$$

The results for the TPM_p protocol were strictly derived for $d_p \to 0$. The corresponding limit, $d_x \to 0$, for the TPM_x protocol would lead to $\sigma_w^{[x]} \to \infty$, which already points out a dramatic difference between these protocols. With the distributions (3.25) we can compute the moment $\overline{w^k}_{[r]} = \int dw\, \wp_w^{[r]} w^k$, and then the mean work $\overline{w}_{[r]} = \int dw\, \wp_w^{[r]} w = w^{[r]}(t_2, t_1)$ and the fluctuation $(\overline{w^2}_{[r]} - \overline{w}_{[r]}^2)^{1/2} = \sigma_w^{[r]}$.

The differences are remarkable and symptomatic. In the TPM_x protocol, the mean momentum p_0 is erased by the first position measurement, thus leading to an average work $w^{[x]}$ whose associated displacement $\Delta_x^{[x]} = -\frac{g\Delta t^2}{2}$ can be very different from the one emerging in the TPM_p protocol, $\Delta_x^{[p]} = \frac{p_0\Delta t}{m} - \frac{g\Delta t^2}{2}$. Most importantly, in the limit as $d_x \to 0$ one has $\sigma_w^{[x]}/\sigma_w^{[p]} \approx \sigma_x/d_x \to \infty$, proving the huge differences implied by each protocol to the work fluctuation. Here we have an odd state of affairs because the two TPM protocols cannot agree about the mean work done on the particle, therefore failing to demonstrate the conservation of energy for this simple model. In other words, the TPM-based stochastic view fails to validate the identity $\overline{\mathcal{K}(t_2) - \mathcal{K}(t_1)} = \overline{\mathcal{V}(t_1) - \mathcal{V}(t_2)}$ in a conservative system.

As far as the work operator (3.10) is concerned, then $W_{\mathrm{E}\to\mathrm{S}}(t_2,t_1)=\Delta E_{\mathrm{S}}=-g\,(t_2-t_1)\;P^{\mathrm{s}}+\frac{mg^2}{2}\,(t_2^2-t_1^2)$ and one readily identify its eigenstates $|p\rangle$ and respective eigenvalues $w_p(t_2,t_1)=\mathrm{f}_g\Delta x$, where $\Delta x=\frac{p_0\Delta t}{m}-\frac{g\Delta t^2}{2}=\Delta_x^{[p]}$. It then follows that the work distribution can be constructed via momentum distribution as

$$\int_{w_1}^{w_2}dw\;\wp_w=\int_{p_1}^{p_2}dp\;\left|\langle p|\psi_0\rangle\right|^2, \tag{3.27}$$

with the change of dummy variables $w=-g\Delta t\,p+\frac{mg^2\Delta t^2}{2}$ and $dw=-g\Delta t\,dp$. We then find

$$\wp_w=\mathcal{G}_w\left(w^{[p]},\sigma_w^{[p]}\right), \tag{3.28}$$

from which we can compute the k-th moment of work, $\langle w^k\rangle=\int dw\,p_w w^k$, and, in particular, $\langle w\rangle=\mathrm{f}_g\Delta x=w^{[p]}$ and $\sigma_w=(\langle w^2\rangle-\langle w\rangle^2)^{1/2}=\sigma_w^{[p]}$. We see from the above results that $\wp_w=\wp_w^{[p]}\neq\wp_w^{[x]}$, which shows that treating work either as an observable or as a stochastic variable whose value is revealed through TPM does not always give the same statistics. An important aspect contributing to the invalidation of the TPM_x protocol is that this approach gives a mean work inconsistent with the classical predictions, which are expected to be retrieved in light of the application of the Ehrenfest theorem to less-than-cubic potentials. Technically, the "incompatibility" of the TPM_x protocol with the other two approaches can be acknowledged to the fact that $[W_{\mathrm{E}\to\mathrm{S}}(t_2,t_1),X(t)]=i\hbar g\Delta t$ whereas $[W_{\mathrm{E}\to\mathrm{S}}(t_2,t_1),P(t)]=0$, relations that can also be rephrased with V and K, respectively. In the latter case, measurements of the internal energy $E_{\mathrm{S}}=K$ (as demanded in the TPM_p protocol) are not able to disturb work states (which can be the initial states in our approach), so that the two approaches are expected to be compatible. However, in the former case, the position measurement introduces a huge momentum fluctuation, which ultimately leads to the elimination of the information about p_0 and σ_x from the statistics. It is noteworthy that the inadequacy of TPM protocols—at least for the present context and purposes—is not exclusively related to the invasive nature of measurements. It also emerges from the assumption that joint probability distributions can be constructed in the form $\mathfrak{p}_{m|n}\mathfrak{p}_n$. Although it has proven useful for thermodynamics approaches, this rationale is not valid in general quantum contexts, as we shall discuss later.

To further illustrate the difficulties underlying the TPM_x approach, we consider the task of computing the mean instantaneous power associated with the gravitational field. Within the operator-based formalism, we can define the instantaneous power observable as $\mathbb{P}(t)=\lim_{\tau\to0}[E_{\mathrm{S}}(t+\tau)-E_{\mathrm{S}}(t)]/\tau$, which, in light of the definition of work and Eq. (3.10), results in

$$\mathbb{P}(t)=\lim_{\tau}\frac{W_{\mathrm{E}\to\mathrm{S}}(t+\tau,t)}{\tau}=-mg\left(\frac{P^{\mathrm{s}}}{m}-gt\right). \tag{3.29}$$

We then readily obtains $\langle\mathbb{P}(t)\rangle=\mathrm{f}_g\left(\frac{p_0}{m}-gt\right)$, which is the traditional "force $\times$ velocity" statement of instantaneous power and the correct classical limit for the model under scrutiny.

Now, resorting to the TPM-based formulas (3.26) we find

$$\overline{\mathbb{P}}_{\mathrm{TPM}_x}(t) = \lim_{\tau\to 0} \frac{\overline{w}_{[x]}(t+\tau,t)}{\tau} = 0, \tag{3.30}$$

$$\overline{\mathbb{P}}_{\mathrm{TPM}_p}(t) = \lim_{\tau\to 0} \frac{\overline{w}_{[p]}(t+\tau,t)}{\tau} = \mathrm{f}_g\left(\frac{p_0}{m} - gt\right). \tag{3.31}$$

Once again the differences are notorious: the TPM_x protocol is unable to reproduce the time dependence expected for the instantaneous power. An important symptom of the conflict already appears in the fact that the TPM_x-based stochastic work is invariant under time translation. Mathematically, $\overline{w}_{[\mathrm{x}]}(t_2+\delta_t, t_1+\delta_t) = \overline{w}_{[\mathrm{x}]}(t_2,t_1)$. Work, however, is not supposed to necessarily be so, because it is not a state variable, that is, it should depend on the "time path". Indeed, we see that $W_{\mathrm{E}\to\mathrm{S}}(t_2+\delta_t, t_1+\delta_t) \neq W_{\mathrm{E}\to\mathrm{S}}(t_2,t_1)$. Even though the TPM_p protocol has incidentally produced results compatible with the operator-based formalism, this does not change the fact that the former approach conceives a sort of "hybrid" view of nature. That is, one assumes, on the one hand, that two-time physical quantities are stochastic variables not describable as quantum mechanical observables, but one does admit, on the other hand, that quantum mechanics can be applied to describe the deterministic time evolution between the contiguous measurements and the associated probability distributions. In contrast, our approach indicates how to accommodate two-time observables in the standard quantum structure.

As briefly reviewed in the previous chapter, schemes for measuring work other than TPM protocols exist [33, 60] where, in general, energy measurements "classicalize" the system state, since they remove quantum coherence and make the energy become an element of reality, in the sense discussed in Section 2.8. Most importantly, the very act of measuring is a relevant source of work and heat which, as such, must not be excluded from the energy balance. In fact, the idea advocated here, that a Heisenberg model for two-time observables should be preferred in mechanical contexts in relation to TPM methods, is not restricted to the concept of mechanical work, as we show next.

3.2.4 Linear and angular displacements: two-time observables

We provide here further illustrations on the differences in treating time variations of physical quantities either as observables or as stochastic variables.

3.2.4.1 Free-particle displacement

Let us define the displacement operator of a free particle as $\delta(t_2,t_1) = X(t_2) - X(t_1) = P^{\mathrm{s}}\Delta t/m$, where m is the mass of the particle and $\Delta t = t_2 - t_1$. The preparation is assumed to be a Gaussian pure state $\rho_0 = |\psi_0\rangle\langle\psi_0|$ with

$$\psi_0(x) = \langle x|\psi_0\rangle = \left(2\pi\sigma_x^2\right)^{-\frac{1}{4}} \exp\left[-\frac{(x-x_0)^2}{4\sigma_x^2} + \frac{ip_0x}{\hbar}\right], \tag{3.32}$$

where $\langle X^{\mathrm{s}}\rangle = x_0$, $\langle P^{\mathrm{s}}\rangle = p_0$, $\sqrt{\langle (X^{\mathrm{s}}_*)^2\rangle} = \sigma_x$, and $X^{\mathrm{s}}_* \equiv X^{\mathrm{s}} - \langle X^{\mathrm{s}}\rangle$. Again, we assume that a position measurement results in a Gaussian state with width d_x (referring to the measurement resolution), and we use $\mathcal{G}_u\left(\bar{u},\sigma\right) = (2\pi\sigma^2)^{-\frac{1}{2}}\exp\left[-\frac{(u-\bar{u})^2}{2\sigma^2}\right]$ for Gaussian functions with width σ and center at $\bar{u}$.

Treating displacement as a stochastic variable implies using a TPM protocol for its determination. The probability density of finding the value x_i in a measurement of x at $t_1 = 0$ reads

$$\wp_{x_i} = \left|\langle x_i|\psi_0\rangle\right|^2 = \mathcal{G}_{x_i}\left(x_0,\sigma_x\right). \tag{3.33}$$

After the measurement is effectively performed, the state reduces to the eigenstate $|x_i\rangle$, expressed as $\langle x|x_i\rangle = \sqrt{\mathcal{G}_x\left(x_i,d_x\right)}$. The next steps consist of unitarily evolving the resulting state with the unitary operator $U_t = e^{-iHt/\hbar}$, where $H = P^2/2m$, and then computing the conditional probability density

$$\wp_{x_f|x_i} = \left|\langle x_f|U_t|x_i\rangle\right|^2 = \mathcal{G}_{x_f}\left(x_i,d_x(t)\right), \tag{3.34}$$

where $d_x(t) = d_x\sqrt{1+(\hbar t/2md_x^2)^2}$. The displacement distribution is given by $\wp_\delta^{\mathsf{TPM}} = \iint dx_i dx_f\, \wp_{x_i}\wp_{x_f|x_i}\delta_{\mathrm{D}}\left[\delta-(x_f-x_i)\right]$, where δ_{D} is the Dirac delta function. The result reads

$$\wp_\delta^{\mathsf{TPM}} = \mathcal{G}_\delta\left(0,d_x(t)\right), \tag{3.35}$$

implying null mean displacement and fluctuation $d_x(t)$. Now, as far as displacement is treated as the observable $\delta(t,0) = P^{\mathrm{s}}t/m$, it is obvious that its probability distribution is directly related to the momentum's, that is,

$$\wp_\delta = \mathcal{G}_\delta\left(\frac{p_0 t}{m},\frac{\sigma_p t}{m}\right), \tag{3.36}$$

which yields the mean displacement p_0t/m and the uncertainty $\sigma_\delta \equiv \sigma_p t/m = \hbar t/2m\sigma_x$. The differences between the two approaches are remarkable. In particular, for the ideal resolution $d_x \to 0$ one has $d_x(t) \cong \hbar t/2md_x \to \infty$, showing that we completely loose the sense of displacement with the TPM statistics. In addition, it is clear that the first measurement in the TPM protocol eliminates any dependence of the result on the initial momentum p_0 and the width σ_x. In contrast, treating displacement as a quantum observable yields an uncertainty $\hbar t/2m\sigma_x$, which can be significantly small for large values of σ_x and/or m. However counter-intuitive it may sound—for one does not expect to find a well defined value of displacement when the positions at 0 and t are completely random—this actually is a fingerprint of two-time quantum observables. In this regard, trajectory-based interpretations of quantum mechanics may help us to make this point. Considering, for example, the predictions of Bohmian mechanics, the trajectories for the system under scrutiny read [128]

$$x(t) = x_0 + \frac{p_0 t}{m} + \left[x(0)-x_0\right]\sqrt{1+\left(\frac{\hbar t}{2m\sigma_x^2}\right)^2}, \tag{3.37}$$

where $x(0)$ defines the initial condition of each particular Bohmian trajectory. In this approach, these trajectories flow side-by-side governed by the quantum potential. Introducing the Ehrenfest time scale $t_E = 2m\sigma_x^2/\hbar$ and considering the long-time regime, we find the displacement

$$x(t) - x(0) \cong \left(\frac{p_0}{m} + \frac{[x(0) - x_0]}{t_E} \right) t, \tag{3.38}$$

which approaches $p_0 t/m$ when t_E is large enough. Therefore, within the Bohmian perspective, it is perfectly fine for a system to have a well defined displacement $(\sigma_\delta \to 0)$ and a highly uncertain position $(\sigma_x \to \infty)$. Interestingly, here we explicitly have the uncertainty relation $\sigma_\delta \sigma_x = \hbar t/2m$.

3.2.4.2 Spin precession

We now provide an illustration involving discrete variables. Consider the task of assessing the variation of the y-component of a spin-$\frac{1}{2}$ angular momentum in the dynamics imposed by $H = \omega S_z$ over the time interval $\left[0, \frac{\pi}{2\omega}\right]$, where ω is the precession frequency [129]. Given the Heisenberg operator $S_y(t) = S_x^{\S} \sin\omega t + S_y^{\S} \cos\omega t$, it follows that treating the mentioned quantity as observable results in

$$\delta S_y = S_y\left(\pi/2\omega\right) - S_y\left(0\right) = S_x^{\S} - S_y^{\S} \doteq \frac{\hbar}{2} \begin{pmatrix} 0 & 1+i \\ 1-i & 0 \end{pmatrix}, \tag{3.39}$$

with eigenvalues $\epsilon\hbar/\sqrt{2}$ and respective eigenvectors $|u_\epsilon\rangle = \left(|0\rangle + \epsilon\, e^{-i\pi/4}\,|1\rangle\right)/\sqrt{2}$, where $\epsilon = \pm 1$. Let us consider the initial state $|\psi_0\rangle = |+\rangle = (|0\rangle + |1\rangle)/\sqrt{2}$. The probability distribution for δS_y then reads

$$\mathfrak{p}_{\delta S_y}(\epsilon) = |\,\langle u_\epsilon|\psi_0\rangle\,|^2 = \tfrac{1}{2}\left(1 + \tfrac{\epsilon}{\sqrt{2}}\right). \tag{3.40}$$

It is noteworthy that to obtain this distribution experimentally one needs to measure a single observable, $S_x^{\S} - S_y^{\S}$, right after the preparation of the pure ensemble $|\psi_0\rangle$. Let us now consider the stochastic-variable approach. The probability of getting $\epsilon\hbar/2$ in a measurement of S_y at $t = 0$ is given by $\mathfrak{p}(\epsilon) = |\,\langle y_\epsilon|\psi_0\rangle\,|^2 = 1/2$, where $|y_\epsilon\rangle = \left(|0\rangle + i\epsilon\,|1\rangle\right)/\sqrt{2}$. The post-measurement state evolved until an instant $t > 0$ reads $|\psi(t)\rangle = \left(e^{-i\omega t/2}\,|0\rangle + i\epsilon\, e^{i\omega t/2}\,|1\rangle\right)/\sqrt{2}$, which for the specific time $t = \pi/2\omega$ reduces to $|\psi(\frac{\pi}{2\omega})\rangle = \left(|0\rangle - \epsilon\,|1\rangle\right)/\sqrt{2}$. The probability of getting $\epsilon'\hbar/2$ in a subsequent measurement of spin is $\mathfrak{p}(\epsilon'|\epsilon) = |\,\langle y_{\epsilon'}|\psi(\frac{\pi}{2\omega})\rangle\,|^2 = 1/2$. The resulting probability distribution is

$$\mathfrak{p}^{\mathsf{TPM}}_{\delta S_y} = \mathfrak{p}(\epsilon'|\epsilon)\mathfrak{p}(\epsilon) = 1/4. \tag{3.41}$$

The divergence between the distributions (3.40) and (3.41) is clear. In particular, with them we find the following mean values:

$$\langle \delta S_y \rangle = \sum_{\epsilon} \left(\frac{\epsilon \hbar}{\sqrt{2}} \right) \mathfrak{p}_{\delta S_y}(\epsilon) = \hbar/2, \tag{3.42}$$

$$\langle \delta S_y \rangle^{\mathrm{TPM}} = \sum_{\epsilon,\epsilon'} \left(\frac{\epsilon' \hbar}{2} \frac{\epsilon \hbar}{2} \right) \mathfrak{p}^{\mathrm{TPM}}_{\delta S_y} = 0. \tag{3.43}$$

We see that the TPM approach predicts null variation for the y-component of spin in the considered time interval, which is unexpected from a semiclassical perspective.

Now that we have analyzed these intuitive examples, we turn to the question on how well-defined work can be.

3.3 Work as a two-time element of reality

In their 1935 paper [113], Einstein, Podolsky, and Rosen (EPR) associated the notion of *element of reality* with the condition of full predictability of a given physical quantity, as we discussed in Section 2.8. According to their criterion, "if, without in any way disturbing a system, we can predict with certainty the value of a physical quantity, then there exists an element of physical reality corresponding to this physical quantity". So, if a spin-$\frac{1}{2}$ particle is prepared in the state $|0\rangle = (|+\rangle + |-\rangle) / \sqrt{2}$, thus implying a null mean-square deviation for the z-component ($\sigma_{S_z} = 0$), then S_z is an EPR element of reality, while S_x is not ($\sigma_{S_x} > 0$). Accordingly, $|0\rangle$ is said to be an S_z state of reality[3].

However tempting it might be, treating a two-time observable as a stochastic variable that becomes an EPR element of reality only via the realization of a TPM protocol actually dismisses the quantum subtleties underlying such an object and is, ultimately, unjustifiable from a fundamental viewpoint. To make this point thoroughly, we consider the two-time operator $C(t_2, t_1) = \frac{1}{2}\{A(t_1), B(t_2)\}$, with $A(t) = \sum_a a\Lambda_a(t)$ and $B(t) = \sum_b b\Lambda_b(t)$ denoting nondegenerate discrete-spectrum observables with respective Heisenberg projectors $\Lambda_{a,b}(t) = \phi_t(\Lambda^{\mathfrak{s}}_{a,b})$. Starting with the mean value $\langle C \rangle (t_2, t_1) = \mathrm{Tr}[C(t_2, t_1)\rho_0]$, one obtains

$$\langle C \rangle (t_2, t_1) = \sum_{a,b} ab \, \mathrm{Tr}[\Lambda_b(t_2)\Gamma_a(t_1)] \, \mathfrak{p}(a, t_1), \tag{3.44}$$

where

$$\Gamma_a(t_1) = \frac{\{\rho_0, \Lambda_a(t_1)\}}{2\mathfrak{p}(a, t_1)}, \qquad \mathfrak{p}(a, t_1) = \mathrm{Tr}[\Lambda_a(t_1)\rho_0]. \tag{3.45}$$

Because $\Gamma_a(t_1) \neq \Lambda_a(t_1)$, one can immediately conclude that

$$\mathrm{Tr}[\Lambda_b(t_2)\Gamma_a(t_1)] \neq \mathfrak{p}(b, t_2|a, t_1) = \mathrm{Tr}[\Lambda_b(t_2)\Lambda_a(t_1)] \tag{3.46}$$

[3] Under the alternative approach put forward by Bilobran and Angelo (BA), described in Section 2.8, it is claimed that a state like $\mathfrak{p}\,|0\rangle\langle 0| + (1-\mathfrak{p})\,|1\rangle\langle 1|$ also implies an element of reality for S_z, even being such that $\sigma_{S_z} > 0$. Although in this case there is a remaining unpredictability concerning this observable, it derives from a classical mixture of well-established elements of reality. For the sake of simplicity, throughout this section we restrict our analysis to the EPR elements of reality.

and $\langle C\rangle\,(t_2,t_1) \neq \sum_{a,b} ab\,\mathfrak{p}(b,t_2|a,t_1)\mathfrak{p}(a,t_1)$. Moreover, even though $\Gamma_a^\dagger = \Gamma_a$ and $\mathrm{Tr}(\Gamma_a) = 1$, one can prove that Γ_a is not positive semidefinite in general and, therefore, is not a quantum state. A simple illustration follows with $\rho_0 = |0\rangle\langle 0|$, $\Lambda_a(t_1) = |+\rangle\langle +|$, and $|\theta\rangle = \cos\theta\ |0\rangle + \sin\theta\ |1\rangle$, for a two-level system. We then find $\langle\theta|\Gamma_a(t_1)|\theta\rangle = \cos\theta\,(\cos\theta + \sin\theta)$, which is negative for $\theta \in \left(\frac{\pi}{2}, \frac{3\pi}{4}\right)$. This shows that conceiving the statistics of the two-time operator $C(t_2,t_1)$ as emerging from the direct product of individual elements of reality a and b weighted by some tentative joint probabilities, such as $\mathrm{Tr}[\Lambda_b(t_2)\Gamma_a(t_1)]\mathfrak{p}(a,t_1)$ (a pseudo joint probability) or $\mathfrak{p}(b,t_2|a,t_1)\mathfrak{p}(a,t_1)$ (the TPM prescription), may be a hasty move in general. Indeed, as we have already seen in Section 3.2.3, a construction like $\mathfrak{p}(b,t_2|a,t_1)\mathfrak{p}(a,t_1)$ may fail to validate energy conservation. Furthermore, we should recall that the covariance function $\frac{1}{2}\langle\{A(t_1),B(t_2)\}\rangle - \langle A(t_1)\rangle\langle B(t_2)\rangle$ and a related witnesses of "time nonlocality" [130] already warn us about the idea of statistics factorability in time.

Thanks to classical mechanics and statistical physics, we got used to the idea that the whole universe is described by a local-in-time state of affairs, with the position and momentum of each particle being elements of reality at each instant of time (realism). Accordingly, one might reject the displacement $x(t_2) - x(t_1)$ of a particle as an element of reality because its constituents $x(t_{1,2})$ do not belong to the same time-local reality state. This view, however, is too restrictive. As we discussed in Section 2.8, there is no problem in viewing $x(t_2) - x(t_1)$ as a two-time element of reality, since it is a relevant physical concept that becomes fully defined as long as one specifies two instants of time. Accordingly, the notion of mean velocity emerges as a relevant element of reality as well, and so does work. This is not to say, however, that the entire segment $x(t_2) - x(t_1)$ of trajectory is an element of reality, although this would be admissible in classical physics. The statement is weaker, as it focuses only on those two specific instants of time. Moreover, there is no need for one to consider displacement as a combination of two elements of reality; once we fix $t_{1,2}$, displacement can be viewed as an "indivisible quantity" (a unit *per se*), with an element of reality $p_0(t_2 - t_1)/m$.

Referring back to the operator $C(t_2,t_1) = \frac{1}{2}\{A(t_1),B(t_2)\}$, one may regard $C(t_2,t_1)$ as an observable in its own right, with its own elements of reality, and not as a mere mix of the observables $A(t_1)$ and $B(t_2)$. To this end, we have to fix $t_{1,2}$, express $C(t_2,t_1)$ in terms of Schrödinger operators, and then diagonalize it for these specific instants of time. Having obtained $C(t_2,t_1)\Lambda_c^i(t_2,t_1) = c\Lambda_c^i(t_2,t_1)$ (with eventual degeneracy $i = 1,2,\cdots,g_c$), we can think of two-time elements of reality c, not necessarily equal to ab, with respective two-time probabilities $\mathfrak{p}(c,t_2,t_1) = \sum_i \mathrm{Tr}[\Lambda_c^i(t_2,t_1)\,\rho_0]$. The preparation $\Lambda_c^i(t_2,t_1)$ guarantees a well defined value for $C(t_2,t_1)$ for the fixed times $t_{1,2}$, that is, a two-time element of reality. This preparation, however, does not ensure that there will be an element of reality for $C(t_4,t_3)$ with $t_{4,3} \neq t_{1,2}$ because $\Lambda_c^i(t_2,t_1)$ will not necessarily be an eigenstate of $C(t_4,t_3)$. As we have illustrated in previous sections, the work operator perfectly fits in this picture, since we can always obtain the eigenvalue relation $W_{\mathrm{E}\to\mathrm{S}}(t_2,t_1)\Lambda_w^i(t_2,t_1) = w(t_2,t_1)\Lambda_w^i(t_2,t_1)$ for some

work projectors $\Lambda_w^i(t_2,t_1)$. In Sections 3.2.1 and 3.2.2, we have found $\Lambda_w(t_2,t_1) = |p\rangle\langle p|$ and $\Lambda_w^i(v\tau,u\tau) = |p_1\rangle\langle p_1| \otimes |p_2\rangle\langle p_2|$ (with high degeneracy), respectively. We remind the reader that these constructions regarded momentum as a discrete variable. In a continuous-variable description, we can think of infinitesimal projectors like $d\Lambda_w(t_2,t_1) = |p\rangle\langle p|\, dp$. This is the approach we employ in what follows.

3.4 A Schrödinger-like picture for work

Arguably, work stands out among the two-time observables because of its fundamental role in the law of conservation of energy. Here we point out another special facet of this concept within the quantum formalism. To this end, it is convenient to rephrase Eq. (3.4) in terms of the Heisenberg power $\mathbb{P}(t) = \phi_t(\mathbb{P}^{\text{s}})$, where $\mathbb{P}^{\text{s}} = \phi_t^*(-\frac{1}{2}\{\dot{X}_i, \partial_{X_i} V_{ij}\})$ is a function of Schrödinger operators. Then, we can write $W_{j\to i}(t_2,t_1) = \mathbb{P}(t_2,t_1)\Delta t$ with the average power

$$\mathbb{P}(t_2,t_1) := \int_{t_1}^{t_2} \frac{dt}{\Delta t}\, \phi_t(\mathbb{P}^{\text{s}}) \equiv \Phi_{t_2,t_1}(\mathbb{P}^{\text{s}}), \tag{3.47}$$

for $\Delta t = t_2 - t_1$. Here we have introduced the time-averaging map Φ_{t_2,t_1} satisfying $\lim_{t_2\to t_1} \Phi_{t_2,t_1} = \phi_{t_1}$ and $\Phi_{t_2,t_1} = \Phi^*_{-t_2,-t_1}$. Of course, not all two-time observables admit a description in terms of this map. Let us consider the continuous-variable spectral decomposition $\mathbb{P}^{\text{s}} = \int d\Lambda_\pi\, \pi$, with orthogonal projectors $d\Lambda_\pi = \Lambda_\pi d\pi$ such that $\Lambda_\pi = |\pi\rangle\langle\pi|$, $d\Lambda_\pi d\Lambda_{\pi'} = \delta_{\pi,\pi'} d\Lambda_\pi$, $\int d\Lambda_\pi = \mathbb{1}$, and $\text{Tr}(d\Lambda_\pi) = 1$. In the jargon introduced previously, $\phi_t(d\Lambda_\pi)$ is a state of reality (an eigenstate) associated with the power $\mathbb{P}(t) = \int \phi_t(d\Lambda_\pi)\pi$. Note that a similar construction applies to all Heisenberg operators. Given the preparation ρ_0, the probability of finding the element of reality π for the power $\mathbb{P}^{\text{s}}$ is $d\mathfrak{p}(\pi) = \text{Tr}(d\Lambda_\pi\, \rho_0)$. The work operator now reads

$$W_{j\to i}(t_2,t_1) = \int \Phi_{t_2,t_1}\left(d\Lambda_\pi\right)\, \pi\Delta t \tag{3.48}$$

and the probability associated with the element of reality $\pi\Delta t$ is given by

$$d\mathfrak{p}(\pi,t_2,t_1) = \text{Tr}\left[\rho_0\, \Phi_{t_2,t_1}\left(d\Lambda_\pi\right)\right]. \tag{3.49}$$

This is a genuine probability since it is nonnegative and $\int d\mathfrak{p}(\pi,t_2,t_1) = 1$. Now we come to the crux: in light of the analogy $\Phi_{t_2,t_1} \rightleftharpoons \phi_t$, the structure of the relations (3.48) and (3.49) becomes closely related to Heisenberg's formalism for one-time operators, like power. This view is strengthened by the fact that we can readily check the validity of the completeness relation $\int \Phi_{t_2,t_1}\left(d\Lambda_\pi\right) = \mathbb{1}$ and the Schrödinger-like formulation $d\mathfrak{p}(\pi,t_2,t_1) = \text{Tr}\left[\Phi^*_{t_2,t_1}(\rho_0)\, d\Lambda_\pi\right]$. Likewise, the mean work

$$\langle W_{j\to i}(t_2,t_1)\rangle = \int d\mathfrak{p}(\pi,t_2,t_1)\, \pi\Delta t = \text{Tr}\left[\rho_0 \Phi_{t_2,t_1}\left(\mathbb{P}^{\text{s}}\Delta t\right)\right] \tag{3.50}$$

also admits a Schrödinger-like formulation in terms of the state

$$\Phi^*_{t_2,t_1}(\rho_0) = \int_{t_1}^{t_2} \frac{dt}{\Delta t} \phi_t^*(\rho_0). \tag{3.51}$$

Note that this is a legitimate quantum state, meaning that it is normalized, Hermitian, and positive semidefinite. Furthermore, it shows us the laborious way[4] through which one can raise the distribution (3.49): in principle, one can determine $\rho(t) = \phi_t^*(\rho_0)$ via quantum state tomography at every instant of time and then compute the average theoretically. An important consequence of such "time mixture" is that the purity of $\Phi_{t_2,t_1}^*(\rho_0)$ is in general smaller than ρ_0's. To explicitly verify this, we use the concavity and the unitary invariance of the von Neumann entropy S, which are respectively written as $S\left(\sum_i p_i\rho_i\right) \geqslant \sum_i p_i S(\rho_i)$ and $S\left(U\rho_i U^\dagger\right) = S(\rho_i)$ for generic states ρ_i, probability distributions p_i, and unitary transformations U. With that, we arrive at $S(\Phi_{t_2,t_1}^*(\rho_0)) \geqslant S(\rho_0)$, with equality holding if, and only if, $\Phi_{t_2,t_1}^*(\rho_0) = \rho_0$ (this occurs, for example, when ρ_0 is a stationary state). It follows that $\Phi_{t_2,t_1}^*(\rho_0)$ typically is a mixed state. This is, however, no different from what we have obtained previously. Referring back to Eq. (3.6), for instance, we see that the mean energy $\mathrm{Tr}\left[\rho_0\phi_{t_i}(H_{\mathrm{S}}^{\mathrm{s}}\otimes\mathbb{1}_{\mathrm{E}})\right]$ equals $\mathrm{Tr}_{\mathrm{S}}\left[\Omega(t_i)H_{\mathrm{S}}^{\mathrm{s}}\right]$, where $\Omega_i = \mathrm{Tr}_{\mathrm{E}}[\phi_{t_i}^*(\rho_0)]$ is, in light of the Stinespring theorem, a mixed state.

The take-away message is as follows. Generic two-time observables cannot be defined in terms of a genuine Schrödinger picture because there exists no sensible notion of two-time state. Yet, quantum mechanical work does admit a formulation in terms of a Schrödinger-like picture, which, however, demands the notion of a time-mixture state. Its definition, Eq. (3.51), clearly implements the time averaging originally codified in the definition of work in Heisenberg's picture. Besides attesting to the overall consistency of our approach, it suggests another way of performing tests of principle in the laboratory.

There is at least one point where the analogy with Heisenberg's formalism for one-time operators does not always apply: Eq. (3.48) is not generally equivalent to the spectral decomposition of work in their states of reality. This is so because $\Phi_{t_2,t_1}(d\Lambda_\pi)$ is not necessarily a $W_{j\to i}(t_2,t_1)$ eigenstate. Nevertheless, this fact does not invalidate the Schrödinger-like view developed above, because Eqs. (3.48)-(3.51) were derived without this assumption. On the other hand, when this condition is fulfilled, a preparation like $\rho_0 = \Phi_{t_2,t_1}(d\Lambda_{\bar{\pi}})$ satisfies $W_{j\to i}(t_2,t_1)\rho_0 = \bar{\pi}\Delta t\rho_0$. Hence, $\langle W_{j\to i}(t_2,t_1)\rangle = \bar{\pi}\Delta t$ and $\langle W_{j\to i}^k(t_2,t_1)\rangle = \langle W_{j\to i}(t_2,t_1)\rangle^k$, meaning that no quantum indefiniteness whatsoever can be associated with work. In this case, work becomes a two-time element of reality.

3.5 Work-energy uncertainty principle

In connection with the previous discussion, here we emphasize that once work is acknowledged as an observable, then one has to abandon the view that it is a mere combination of

[4] In Section 3.2.3, we have shown how to build the work probability distribution starting with the expansion of the Heisenberg work operator in terms of a resulting Schrödinger operator, that is, $W_{\mathrm{E}\to\mathrm{S}}(t_2,t_1) \equiv O^{\mathrm{s}}$. With that, the task is directly accomplished through the construction of the probability distribution associated with O^{s}. In general, however, this procedure can be very laborious as well, for O^{s} is expected to be a joint observable demanding nonlocal measurements.

elements of reality. More importantly, quantum mechanics allows work to be an element of reality even when its constituent terms are not. This can be appreciated by use of uncertainty relations. Let $\sigma_O = \sqrt{\langle O_*^2 \rangle}$, with $O_* \equiv O - \langle O \rangle$, be the quantum uncertainty of a given Heisenberg operator O, and $W_{21} = H_2 - H_1$ is a shorthand for the resultant work operator $W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1)$ given in Eq. (3.6), where $H_i \equiv H_{\mathrm{S}}(t_i)$. Via the weak version of the uncertainty principle, we have $\sigma_{W_{12}}\sigma_{H_i} \geq \frac{1}{2}|\langle [W_{21}, H_i] \rangle|$. Since $[W_{21}, H_1] = [H_2, H_1] = [W_{21}, H_2]$, one finds

$$\sigma_{W_{21}} \left(\sigma_{H_1} + \sigma_{H_2}\right) \geq |\langle [H_1, H_2] \rangle| \,. \tag{3.52}$$

This (two-time) uncertainty relation shows that, excluding very particular states like $\rho_0 = \mathbb{1}/d$, with $d = \dim(\mathbb{H}_{\mathrm{S}} \otimes \mathbb{H}_{\mathrm{E}})$, which implies $\langle [H_1, H_2] \rangle = 0$, the general situation is such that whenever the energy operators do not commute at different times, one cannot produce states ensuring arbitrarily small uncertainties for work and the initial and final energies simultaneously[5]. A direct illustration of this result was presented in Section 3.2.1, where via the preparation of a momentum eigenstate we had $\sigma_{W_{21}} \to 0$ and $\sigma_{V_i} \to \infty$, with V_i being the gravitational potential energy and $[V_1, V_2] = i\hbar\Delta t/m$. In this case, work due to the gravitational potential is an element of reality, while the energies at times $t_{1,2}$ are not. Rather than seeing all this as a drawback for the notion of work operator [63]—an attitude that is ultimately based on classical lines of thought— here we defend that this actually is a subtle manifestation of a truly quantum notion of work.

3.6 Take-away messages

The claim "work is not an observable" [31] has been derived from the premise that fluctuation theorems are correct. This is of course a good working hypothesis in several contexts, but it is debatable whether one should stick to this perspective in order to have a fundamental theory of microscopic mechanical systems. Should we add to the axiomatic structure of quantum mechanics the assumption that two-time variables, such as work, displacement, and velocity, are to be treated as stochastic variables? Here we answered this question in the negative for a genuinely quantum mechanical context involving conservative autonomous few-particle systems. Not only did we show that work can be technically viewed as a quantum observable, but gave some examples in which the TPM-based stochastic view greatly deviates from the expected semiclassical results. Our results do not eliminate the operational relevance of the stochastic view for general contexts, but they show that it is not unavoidable from a fundamental viewpoint.

Our proposal for the concept of quantum mechanical work requires an updating of the common view that physical concepts refer to a time-local state of affairs. In fact, this cannot

[5] Of course, relation (3.52) is not an exclusiveness of the pair work-energy. It is easy to show that for any operator $\Gamma_{21} = A_1 + A_2$, one can prove that $\sigma_{\Gamma_{21}}(\sigma_{A_2} + \sigma_{A_1}) \geq |\langle [A_1, A_2] \rangle|$. In Sections. 3.2.1 and 3.2.4, the problem regarding the displacement of a free particle was analyzed. By preparing the system in a momentum eigenstate, we have $\sigma_{\delta_{21}} \to 0$ whereas $\sigma_{X_i} \to \infty$.

be the case even within the classical paradigm. As we have shown, once we conceive that a two-time observable can be described as a Heisenberg operator, with its fixed-time expansion in terms of Schrödinger operators and its related eigenbasis, then we learn how to derive the corresponding statistics, without in any way resorting to non-quantum methods. The whole characterization of the concept as a genuine quantum entity thus follows: the work done on a system (i) has a well-defined spectrum (eventually quantized), (ii) can be prepared as an element of reality via specific measurements, (iii) has an intrinsic quantum fluctuation, and (iv) satisfies an uncertainty relation with energy.

In the sequence, we use our QM work definition and the induced notion of two-time observables to discuss how the conservation of energy can be guaranteed as an element of reality. Also to analyze the effect that a projective measurement has on the energetic balance of a given system.

4 Energy conservation, quantum measurements, and two-time observables

As pointed out in Section 2.7, there is still no consensus regarding the conservation laws in quantum mechanics. Three key difficulties can be mentioned: (i) it is not yet clear how energy measurement-induced disturbance can be accounted; (ii) conservation laws are still debatable in quantum mechanics and (iii) there is no standard well-established recipe to compute probability distributions for two-time quantities. In the previous chapter, we proposed a form of solving item (iii). Our aim in the present chapter is to analyze (i) and (ii), given our answer to (iii). With the results presented in this chapter, we hope to highlight the important connection between the concept of physical reality, measurements and conservation laws.

4.1 Minimal, necessary conditions for two-time measurement protocols

How can we be sure whether the law of conservation of energy is valid in a quantum scenario? If for a round of the experiment, we somehow verify that the energy is not conserved, can we guarantee that this violation is due to interference of the apparatus in the energy balance of the system? As discussed in Section 2.7, these questions are hard to analyze and several approaches have been proposed to answer them.

Here we propose a different strategy, inspired by the article [37]. Instead of analyzing situations in which there are apparent violations of the law of conservation of energy and study them in detail, we aim at proposing *minimal* conditions so as to attest whether the energy can be said to be or not conserved. In this sense, we do not assume for now any specific protocol for the energy variation detection but we search for minimal criteria which must be satisfied for one to be in consonance with the law of conservation of energy. Therefore, throughout this section, we are not assuming, *a priori*, two-time observables treated in the previous chapter nor any other specific approach.

We conceive an universe U whose initial state is described by the operator ρ, subjected to an unitary dynamics U governed by the Hamiltonian operator

$$H = H_{\mathrm{A}} + H_{\mathrm{R}} \tag{4.1}$$

where H_{A} refers to the energy of part A and H_{R} refers to the energy of the rest $\mathrm{R} = \mathrm{U} - \mathrm{A}$. We also consider the Heisenberg picture as in the previous chapter, so that the relation $O(t) = U_t^\dagger O^{\mathrm{s}} U_t$ is valid for any Schrödinger operator O^{s}. It is crucial to highlight here that we do not demand H_{A} to necessarily be an internal energy operator. Here, we are just dividing our Hamiltonian into two convenient Hermitian parts H_{A} and H_{R}. Therefore,

we may consider the example of the elastic potential case in Subsection 3.2.2, where $H = P_1^2/2m_1 + \frac{k}{2}(X_2 - X_1)^2 + P_2^2/2m_2$, in many different scenarios: we could, for instance, assume either $H_{\rm A} = P_1^2/2m_1$ or $H_{\rm A} = P_1^2/2m_1 + \frac{k}{4}(X_2 - X_1)^2$, so that the energy of the rest would be given as $H_{\rm R} = \frac{k}{2}(X_2 - X_1)^2 + P_2^2/2m_2$ and $H_{\rm R} = \frac{k}{4}(X_2 - X_1)^2 + P_2^2/2m_2$, respectively. As a result, in the former case, we are interested in the kinetic energy of particle 1, while in the latter, we are interested also in part of the potential energy.

Consider now a measurement protocol $\mathbb{M}$ that describes measurements and the resulting statistics of *variations* of energy[1]. We denote by $\mathbb{M}_{\rm X}(t_2, t_1) \equiv \mathbb{M}_{\rm X}(H_{\rm X}^{\rm s}, U, t_2, t_1)$ as the protocol which assess the energy variations of the system ${\rm X} \in \{{\rm A}, {\rm R}\}$ during the interval $[t_1, t_2]$. Here, in analogy with [37], we are not yet fixing the characteristics of the protocol $\mathbb{M}_{\rm X}(t_2, t_1)$ but we assume that it depends on $H_{\rm X}^{\rm s}$, the dynamics U of the universe, and the interval $[t_1, t_2]$. Regarding $\mathbb{M}_{\rm X}(t_2, t_1)$, we can raise the probability distribution $\wp_{\rm X}(\Delta, t_2, t_1)$ referring to the event in which the system X has its energy changed by an amount Δ during the interval $[t_1, t_2]$. We thus enunciate the following necessary condition we expect $\mathbb{M}_{\rm X}$ to satisfy for any part X:

Condition 4.1. *(Reality) If the initial state ρ is an eigenvector of both $H_{\rm X}(t_1)$ and $H_{\rm X}(t_2)$, with respective eigenvalues $e_{\rm X}$ and $e'_{\rm X}$, then the measurement protocol $\mathbb{M}_{\rm X}$, when applied for ρ, can only result in $e'_{\rm X} - e_{\rm X}$.*

We call this condition the reality condition, as it can be restated in terms of EPR notion of element of reality: *if the energies of a given system* X *are EPR elements of reality at times t_1 and t_2 then their difference should be too.*

The reality condition then establishes a necessary criterion that a consistent measurement protocol $\mathbb{M}_{\rm X}$ has to satisfy. Surely, if we know with a hundred percent certainty, the energies at times $t_{1,2}$, how can we not be sure about their difference? Notice that we do not demand $\mathbb{M}_{\rm X}$ to give a precise value *only* for the scenarios prescribed in the reality condition; it is just for the special cases described in the condition that we demand it so. Therefore, if ρ is not an eigenvector of either $H_{\rm X}(t_1)$ or $H_{\rm X}(t_2)$, then the reality condition does not restrict $\mathbb{M}_{\rm X}$ in any way; it is in this sense that it is a necessary condition and not sufficient. With the reality condition stated, we are now in position to introduce a necessary condition for the conservation of energy to hold:

Condition 4.2. *(Weak condition for energy conservation) The protocol $\mathbb{M}_{\rm X}$ is said to preserve the law of conservation of energy only if, for any real value Δ, the induced probability distributions satisfy*

$$\wp_{\rm A}(\Delta, t_2, t_1) = \wp_{\rm R}(-\Delta, t_2, t_1). \tag{4.2}$$

This weak condition implements the classical perspective encoded in Eq. (2.56) of Section 2.7. We call this condition weak, in the sense that we do not care about specific

[1] $\mathbb{M}$ can in fact be constructed from the POVMs succinctly reviewed in Section 2.7. For more details on specifications of these protocols, we refer the reader to [37, 60, 84, 99] and references therein.

rounds of the experiment implemented by $\mathbb{M}$ since $\mathbb{M}$ can be such as to severely disturbs the system. Indeed, from the WAY theorem (see Section 2.7), we already know that a protocol $\mathbb{M}$ may alter significantly the state of the system being measured, so that for a specific round, an apparent violation of energy may occur. The weak energy conservation condition, on the other hand, is designed to be immune to these one-round measurement effects, as it considers probabilities instead of individual outcomes.

We proposed both the weak conservation together with the reality condition in order to establish the minimal necessary conditions for us to attest whether a measurement protocol violates the law of conservation of energy. Therefore, if part of the energy of a given closed universe surely varies an amount Δ, then a protocol that predicts no violation of the conservation of energy must predict a variation by the same amount to the rest of the universe. In other words, the protocol satisfy both of the described conditions. If, on the other hand, a protocol is such that one out of the two conditions is not satisfied, than we can definitely state that energy conservation is violated for that protocol. The conditions are thus not designed to attest whether a protocol *validates* the energy conservation, but to probe when violations occur. Consequently, these conditions can be used to test many of the approaches to measuring energy changes and see if they violate the law of conservation of energy. This is, in fact, one of our goals for future research projects. Interestingly, it can be shown that the TPM procedure, when adapted to the autonomous scenario of (4.1), satisfy the reality condition, but not weak conservation one. This can be demonstrated using the example of Section 3.2.3. With the form (4.1), where $H_{\mathrm{A}} = H_{\mathrm{S}} = P^2/2m$ and $H_{\mathrm{R}} = mgX$, we showed in Section 3.2.3 that for a Gaussian state $\wp_{\mathrm{A}}(\Delta, t_2, t_1) \neq \wp_{\mathrm{R}}(-\Delta, t_2, t_1)$, so that the weak conservation condition is not satisfied. However, if the initial state is a momentum eigenvector (or a normalized version of it), then the TPM_p procedure will be in consonance with the reality condition.

4.2 Two-time quantum observables and conservation of energy

In the same way that we could describe work as a two-time quantum observable, we can assign to the variation of energy of a given part of the system $\mathrm{X} \in \{\mathrm{A}, \mathrm{B}\}$ a Heisenberg quantum observable $\Delta H_{\mathrm{X}}(t_2, t_1) = H_{\mathrm{X}}(t_2) - H_{\mathrm{X}}(t_1)$. With $\Delta H_{\mathrm{X}}(t_2, t_1)$, we are thus able to describe its statistics in accordance with quantum mechanics axioms, as we showed in the previous chapter: we can find out a Schrödinger observable B^{s} that commutes with $\Delta H_{\mathrm{X}}(t_2, t_1)$, so that by measuring B^{s} we can raise the statistics of the variation of energy of X, computing the probability

$$\wp_{\mathrm{X}}(\delta_j^{\mathrm{X}}, t_2, t_1) = \mathrm{Tr}\left(|\delta_j^{\mathrm{X}}\rangle\langle\delta_j^{\mathrm{X}}|\,\rho\right) \tag{4.3}$$

where[2] $|\delta_j^{\mathrm{X}}\rangle$ are eigenvectors of both $\Delta H_{\mathrm{X}}(t_2,t_1)$ (with corresponding eigenvalues δ_j^{X}) and B^{s}. A measurement protocol $\mathbb{M}^{\mathrm{obs}}$ specified by this procedure is naturally dependent only on the times $t_{1,2}$, the unitary evolution and the form of H_{X}.

As we are assuming a universe whose dynamics is described by (4.1), we know that the observable $\Delta H_{\mathrm{A}}(t_2,t_1)$ is equal to $-\Delta H_{\mathrm{R}}(t_2,t_1)$, since $\Delta H(t_2,t_1)=0$. Therefore, the eigenvectors satisfy the relation $|\delta_j^{\mathrm{A}}\rangle = |\delta_j^{\mathrm{R}}\rangle$, with the respective eigenvalues $\delta_j^{\mathrm{A}} = -\delta_j^{\mathrm{R}}$. As a result, the weak conservation condition follows trivially when we consider $\mathbb{M}^{\mathrm{obs}}$, since for any admissible value $\delta_j^{\mathrm{A}} = -\delta_j^{\mathrm{R}}$, it follows that

$$\begin{aligned}\wp_{\mathrm{S}}(\delta_j^{\mathrm{A}},t_2,t_1) &= \mathrm{Tr}\left(|\delta_j^{\mathrm{A}}\rangle\langle\delta_j^{\mathrm{A}}|\,\rho\right) = \mathrm{Tr}\left(|\delta_j^{\mathrm{R}}\rangle\langle\delta_j^{\mathrm{R}}|\,\rho\right)\\ &= \wp_{\mathrm{R}}(\delta_j^{\mathrm{R}},t_2,t_1) = \wp_{\mathrm{R}}(-\delta_j^{\mathrm{A}},t_2,t_1).\end{aligned} \tag{4.4}$$

Moreover, if a state ρ is an eigenvector of both $H_{\mathrm{X}}(t_1)$ and $H_{\mathrm{X}}(t_2)$ with corresponding eigenvalues e_{X} and e'_{X}, then ρ is also an eigenvector of $\Delta H_{\mathrm{X}}(t_2,t_1)$ with eigenvalue $e'_{\mathrm{X}} - e_{\mathrm{X}}$, so that the reality condition is also satisfied. As a result, an observable-like approach ($\mathbb{M}^{\mathrm{obs}}$) for variations of energy does not violate the conditions described in the previous section.

Taking into account the context of work-energy uncertainty relation in Section 3.5, we can also show that a stronger form of energy conservation can be validated using a two-time observable protocol $\mathbb{M}^{\mathrm{obs}}$. Indeed, if we prepare a state $\rho = |\delta_j^{\mathrm{A}}\rangle\langle\delta_j^{\mathrm{A}}|$, then the variation of energy of A is known to be δ_j^{A}, even if the energies at times $t_{1,2}$ are ill-defined. In this case, which is not envisaged in the reality condition, the conservation law is also guaranteed exactly, since $\rho = |\delta_j^{\mathrm{A}}\rangle\langle\delta_j^{\mathrm{A}}| = |\delta_j^{\mathrm{R}}\rangle\langle\delta_j^{\mathrm{R}}|$, with $\delta_j^{\mathrm{R}} = -\delta_j^{\mathrm{A}}$. Indeed, in every scenario in which H_{A} surely varies by a certain amount of energy then, when considering $\mathbb{M}^{\mathrm{obs}}$, H_{R} varies by the negative of the same amount.

Using the two-time observable perspective, implemented by $\mathbb{M}^{\mathrm{obs}}$, we can show that the law of conservation of energy emerges naturally as an EPR element of reality. The fact that $\Delta H = 0$ already directly implies, for any preparation ρ, that the conservation of the total energy is an EPR element of the physical reality, that is

$$\langle\Delta H\rangle = \sigma_{\Delta H} = 0 \qquad \text{(total energy conservation)}. \tag{4.5}$$

However, since ρ need not be an eigenstate of H, it follows that, *although surely conserved in time, the total energy is not readily implied to be an element of reality*. Now, suppose once again that ρ is an eigenstate of ΔH_{A}. Because $\Delta H_{\mathrm{R}} = -\Delta H_{\mathrm{A}}$, one has $\sigma_{\Delta H_{\mathrm{R}}} = \sigma_{\Delta H_{\mathrm{S}}} = 0$. Therefore, if the variation of energy ΔH_{A} is an element of reality, then the energy change of the rest of the universe will also be. All this illustrates the formal ground on which the law of conservation of energy is established within our approach.

We could consider A to be a system of interest S whose internal energy would therefore be $H_{\mathrm{A}} = H_{\mathrm{S}}$, so that ΔH_{A} would account for the QM work done by the rest of the universe

[2] We can extend this formalism for the continuum basis and unbounded operators cases, where $|\delta_j^{\mathrm{X}}\rangle\langle\delta_j^{\mathrm{X}}|$ is substituted by a more general projection operator. We here consider the discrete case seeking simplicity.

on A. All the discussions presented in this section could then be extended to this scenario. Also, R may contain a bath, another system equal to A, interacting with it or any other type of system. In the sequence, we consider a scenario in which R contains an apparatus, so as to characterize its role on the energetic balance.

4.3 The measurement disturbance

In order to account for the disturbance and the energy transference of a measurement apparatus to a given system, we must include it in the dynamical description of the universe U analyzed. Otherwise, even though we can evaluate some energy change in the system, we cannot fully characterize the nature of this energy exchange, thus not knowing where the energy comes from or where did it go. In this sense, we consider an initial preparation ρ of a system of interest S interacting with a measurement apparatus M by means of a unitary $U^{\mathrm{m}} = \exp\left[-(it/\hbar)H_{\mathrm{SM}}\right]$ dynamics prescribed by the autonomous Hamiltonian

$$H_{\mathrm{SM}} = H_{\mathrm{S}} + V_{\mathrm{SM}} + H_{\mathrm{M}}, \tag{4.6}$$

where V_{SM} accounts for an interaction between S and E. The whole system is depicted in Fig. 4.1.

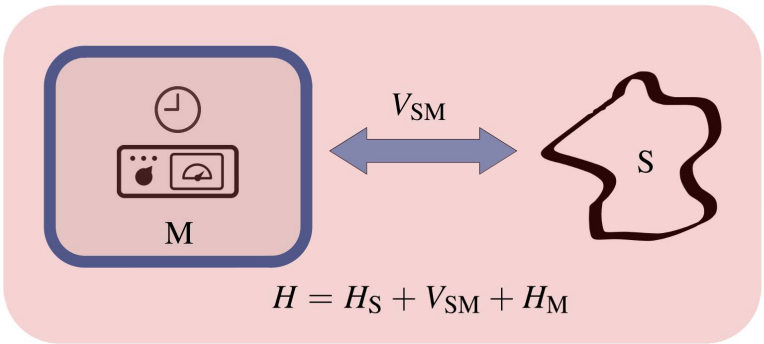


Figure 4.1 – Schematic representation of a universe U composed of an arbitrary system of interest S and the measurement apparatus M. The universe U dynamics is governed by Eq. (4.6), describing the perspective of an external observer.

As we aim to consider a scenario in which the whole system dynamics is autonomous, we assume that the apparatus may contain an autonomous clock, in the same way as discussed in [109]. The transference of energy from the apparatus to S can be fully characterized by the QM work:

$$W_{\mathrm{M}\to\mathrm{S}}(t_2, t_1) = H_{\mathrm{S}}(t_2) - H_{\mathrm{S}}(t_1) = (U^{\mathrm{m}}_{t_2})^{\dagger} H^{\mathrm{s}}_{\mathrm{S}} U^{\mathrm{m}}_{t_2} - (U^{\mathrm{m}}_{t_1})^{\dagger} H^{\mathrm{s}}_{\mathrm{S}} U^{\mathrm{m}}_{t_1} \tag{4.7}$$

so that, given an initial state ρ, one may raise the statistics of the operator $W_{\mathrm{M}\to\mathrm{S}}(t_2, t_1)$ in the same way as described in the previous chapter. Notice that we did not need to add to our

description any other ingredient external to quantum mechanics to characterize the energy exchange with the apparatus, such as the notion of conditional energy or any assumption concerning energy pre-determination [78,84]. Here, we just have a special case, in which the external system is specified as a measurement apparatus. Moreover, the same conditions for the conservation of energy discussed in the previous sections should be satisfied for the measurement apparatus here, so that, by taking $H_{\mathrm{A}} = H_{\mathrm{S}}$ and $H_{\mathrm{R}} = V_{\mathrm{SM}} + H_{\mathrm{M}}$, we have that whenever the internal energy of S is certain to change by an specific amount, then the sum of coupling term with the energy of the apparatus (including its attached clock) must change by the same amount; energy does not vanish or come out from nowhere.

Now, we can explore some interesting signatures of a measurement apparatus. First, it is expected that after a time t_{M}, the apparatus is able to implement the measurement of an observable $A_{\mathrm{S}} \otimes \mathbb{1}_{\mathrm{M}}$ of the system of interest. It is reasonable then to expect that, if the measurement is perfect in the sense that its action on S reduces to strongly measure A_{S}, then the evolved state $\rho(t_{\mathrm{M}}) = U^{\mathrm{m}}_{t_{\mathrm{M}}} \rho (U^{\mathrm{m}}_{t_{\mathrm{M}}})^{\dagger}$ satisfies

$$\rho_{\mathrm{S}}(t_{\mathrm{M}}) = \mathrm{Tr}_{\mathrm{M}}\left(\rho(t_{\mathrm{M}})\right) = \Phi_{A_{\mathrm{S}}}(\rho_{\mathrm{S}}) \tag{4.8}$$

where $\rho_{\mathrm{S}} = \mathrm{Tr}_{\mathrm{M}}(\rho)$ is the initial reduced state and

$$\Phi_{A_{\mathrm{S}}}(\rho) = \sum_k (A_{\mathrm{S}k} \otimes \mathbb{1}_{\mathrm{M}}) \rho (A_{\mathrm{S}k} \otimes \mathbb{1}_{\mathrm{M}}), \tag{4.9}$$

with the projectors $A_{\mathrm{S}k}$ satisfying the relation $A_{\mathrm{S}} = \sum_k a_k A_{\mathrm{S}k}$. Notice that, since we are assuming the role of an external observer describing the $\mathrm{S}+\mathrm{M}$ dynamics, then even though the outcome in the apparatus is presumed to be unique, we cannot access it. Therefore, the best description we can give about of the state of the system is (4.8). Note that nothing prevents this result to follow from first principles by specifying $V_{\mathrm{SM}} + H_{\mathrm{M}}$ and the initial state accordingly. In line with the discussion of Section 2.8, Eq. (4.8) states that the physical quantity A_{S} is a BA element of the physical reality after the measurement. Therefore, even though the apparatus is measuring the system and we, as external observers, cannot access the result of its measurement, we can be sure that A_{S} is well-defined after a time t_{M}. Given that the condition (4.8) is satisfied, we can show that

$$\begin{aligned} \langle W_{\mathrm{M}\to\mathrm{S}}(t_{\mathrm{M}}, 0) \rangle &= \mathrm{Tr}\left[\rho (U'^{\dagger}_{t_{\mathrm{M}}} H^{\mathrm{s}}_{\mathrm{S}} U'_{t_{\mathrm{M}}} - H^{\mathrm{s}}_{\mathrm{S}})\right] = \mathrm{Tr}\left[(U'_{t_{\mathrm{M}}} \rho U'^{\dagger}_{t_{\mathrm{M}}} - \rho) H^{\mathrm{s}}_{\mathrm{S}}\right] \\ &= \mathrm{Tr}_{\mathrm{S}}\left[(\Phi_{A_{\mathrm{S}}}(\rho_{\mathrm{S}}) - \rho_{\mathrm{S}}) H^{\mathrm{s}}_{\mathrm{S}}\right], \end{aligned} \tag{4.10}$$

so that, by use of the Cauchy-Schwartz inequality [129, 131, 132], we have

$$|\, \langle W_{\mathrm{M}\to\mathrm{S}}(t_{\mathrm{M}}, 0) \rangle \,| \leq \| \Phi_{A_{\mathrm{S}}}(\rho_{\mathrm{S}}) - \rho_{\mathrm{S}} \|_2 \| H^{\mathrm{s}}_{\mathrm{S}} \|_2, \tag{4.11}$$

where $\|O\|_2 = \sqrt{\mathrm{Tr}(O^{\dagger} O)}$ denotes the Hilbert-Schmidt norm of operator O. Moreover, given the relation $\|O\|_2 \leq \|O\|_1$ between the Hilbert-Schmidt norm and the Shatten 1-norm

$\|O\|_1 = \mathrm{Tr}(\sqrt{O^\dagger O})$ [133], and the inequality (commonly referred to as quantum Pinsker inequality [133, 134])

$$\|\rho' - \rho''\|_1 = \|\rho'' - \rho'\|_1 \leq \sqrt{2\, S(\rho'||\rho'')}, \tag{4.12}$$

where $S(\rho'||\rho'')$ is the relative entropy of arbitrary states ρ', ρ'', then it follows that

$$\|\Phi_{A_\mathrm{S}}(\rho_\mathrm{S}) - \rho_\mathrm{S}\|_2 \leq \|\Phi_{A_\mathrm{S}}(\rho_\mathrm{S}) - \rho_\mathrm{S}\|_1 \leq \sqrt{2\, S(\rho_\mathrm{S}||\Phi_{A_\mathrm{S}}(\rho_\mathrm{S}))}. \tag{4.13}$$

Inserting (4.13) in (4.11), the following fundamental bound on the transference of energy due to the action of the measurement can be deduced:

$$|\,\langle W_{\mathrm{M}\to\mathrm{S}}(t_\mathrm{M}, 0)\rangle\,| \leq \sqrt{2\, \mathcal{I}_{A_\mathrm{S}}(\rho_\mathrm{S})}\|H^\mathrm{s}_\mathrm{S}\|_2. \tag{4.14}$$

Here, as in Section 2.8, $\mathcal{I}_{A_\mathrm{S}}(\rho_\mathrm{S}) = S(\rho_\mathrm{S}||\Phi_{A_\mathrm{S}}(\rho_\mathrm{S}))$ is used to denote the measure of irreality of the reduced state ρ_S, with respect to the observable A_S.

There are at least two possible forms of interpreting the bound (4.14). On the one hand, $\mathcal{I}_{A_\mathrm{S}}(\rho_\mathrm{S})$ is the BA measure of irreality of A_S with respect to the observable A_S. In this direction, a "perfect" measurement can only alter the energy of a system S if the system has a certain amount of A_S irreality. In accordance with this view, *the degree of* A_S *undefiniteness bounds the energy transfer imposed by the measurement on* S. On the other hand, $\mathcal{I}_{A_\mathrm{S}}(\rho_\mathrm{S})$ can be taken as a measure of coherence [114] (as it accounts for the distance between ρ_S and its incoherent version $\Phi_{A_\mathrm{S}}(\rho_\mathrm{S})$). In this instance, it is the amount of A_S coherence encoded in the preparation ρ_S that bounds the energy transfer.

Let us now consider the system depicted in Fig. 4.2(a). In this case, the autonomous Hamiltonian operator is given by

$$H_\mathrm{SME} = H_\mathrm{S} + V_\mathrm{SM} + H_\mathrm{M} + V_\mathrm{SE} + H_\mathrm{E} \tag{4.15}$$

where we add an external system E (not necessarily an apparatus) interacting only with the system S by means of V_SE. The unitary dynamics induced by H_SME shall be simply denoted as $U = \exp\left[-(it/\hbar)H_\mathrm{SME}\right]$. In this scenario, the total QM work done by M and E on S is in general computed as

$$W_{\mathrm{ME}\to\mathrm{S}}(t_2, t_1) = H_\mathrm{S}(t_2) - H_\mathrm{S}(t_1) = U^\dagger_{t_2} H^\mathrm{s}_\mathrm{S} U_{t_2} - U^\dagger_{t_1} H^\mathrm{s}_\mathrm{S} U_{t_1}. \tag{4.16}$$

If the interaction between the system and the apparatus is well-defined and based on fundamental physical principles, then work done exclusively by the apparatus M can be computed as (see Subsection 3.1)

$$W_{\mathrm{M}\to\mathrm{S}} = \int_{t_1}^{t_2} dt\, \frac{[H_\mathrm{S}(t), V_\mathrm{SM}(t)]}{i\hbar} \tag{4.17}$$

for any initial preparation of the whole system $\mathrm{S} + \mathrm{E} + \mathrm{M}$. Therefore, the energetic disturbance caused by the measurement and its underlying statistics can be fully determined by $W_{\mathrm{M}\to\mathrm{S}}$. Alternatively, if the interaction V_SE implements a fundamental physical interaction, then an equation analogous to (4.17) can be written for $W_{\mathrm{E}\to\mathrm{S}}$, so that

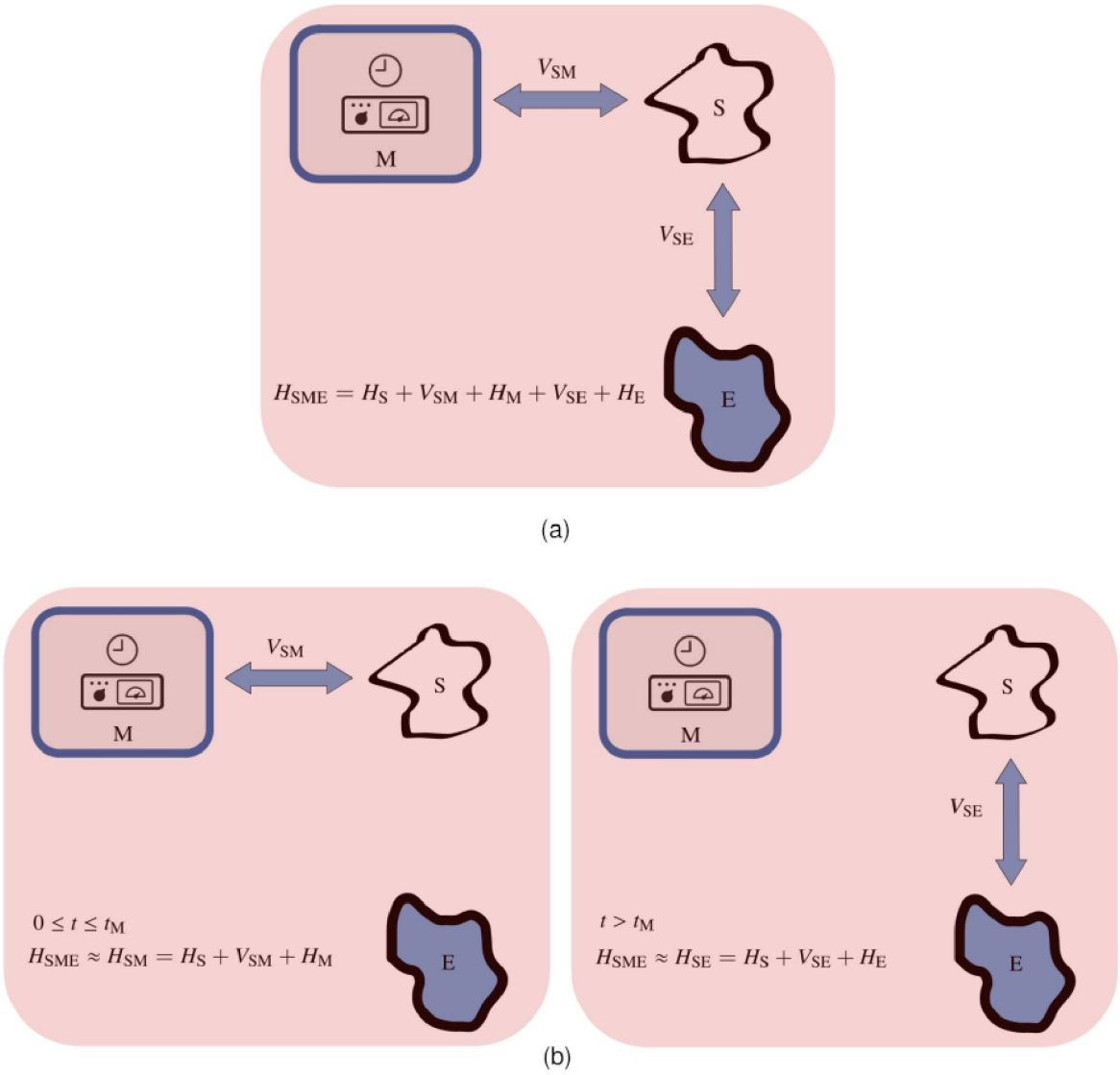


Figure 4.2 – The apparatus M and system of interest S depicted in Fig. 4.1 now are allowed to interact with another arbitrary external system E. In figure (a), only S interacts with E and their dynamics is generally described by the Hamiltonian (4.15). In the more restrict scenario depicted in (b), S interacts only with the apparatus during the interval $[0, t_{\mathrm{M}}]$, so that the measurement takes place and the measured quantity becomes a BA element of reality; after time t_{M} both systems S and E interacts, so that E can do work on S. In the case (b), both the amount of energy transferred during the measurement and work done after the measurement are bounded by the initial irreality of the measured quantity, in accordance with (4.20) and (4.23), respectively.

$W_{\mathrm{M}\to\mathrm{S}} = W_{\mathrm{ME}\to\mathrm{S}} - W_{\mathrm{E}\to\mathrm{S}}$ can be considered for a full statistical description of the energetic disturbance induced solely by the measurement.

Now, to discuss the scenario depicted in Fig. 4.2(b), let us consider the following assumptions:

1. We "configure" the apparatus clock so that the measurement of an observable $A_{\mathrm{S}} \equiv A_{\mathrm{S}} \otimes \mathbb{1}_{\mathrm{M}} \otimes \mathbb{1}_{\mathrm{E}}$ of S will take place after a time t_{M}, from which the apparatus interaction with S is negligible;

2. The interaction term V_{SE} starts to be significantly relevant for [3] $t \approx t_{\mathrm{M}}$.

Roughly, the idea behind these hypotheses is that there is an interval in which only the measurement will take place, whereas, after this time, the apparatus practically does not interact with S and the interaction between S and E becomes relevant. Consequently, we expect that for any time $t \geq t_{\mathrm{M}}$, the unitary dynamics of the whole $\mathrm{S}+\mathrm{E}+\mathrm{M}$ system can be decoupled as $U_t = U_t^{\mathrm{e}} U_{t_{\mathrm{m}}}^{\mathrm{m}}$, where $U_t^{\mathrm{e}} = \exp\left[-(i(t-t_{\mathrm{m}})/\hbar)H_{\mathrm{SE}}\right]$ and $U^{\mathrm{m}} = \exp\left[-(it/\hbar)H_{\mathrm{SM}}\right]$, with $H_{\mathrm{SE}} = H_{\mathrm{S}} + V_{\mathrm{SE}} + H_{\mathrm{E}}$ and H_{SM} defined in (4.6). As a result, the reduced state $\rho_{\mathrm{SE}} = \mathrm{Tr}_{\mathrm{M}}(\rho)$ is expected to satisfy the following relations:

$$\rho_{\mathrm{SE}}(t) = \rho_{\mathrm{SE}}(t_{\mathrm{M}}) = \Phi_{A_{\mathrm{S}}}(\rho_{\mathrm{SE}}), \quad \text{for } t \approx t_{\mathrm{M}} \tag{4.18a}$$

$$\rho_{\mathrm{SE}}(t) = U_t^{\mathrm{e}} \rho_{\mathrm{SE}}(t_{\mathrm{M}})(U_t^{\mathrm{e}})^\dagger = U_t^{\mathrm{e}} \Phi_{A_{\mathrm{S}}}(\rho_{\mathrm{SE}})(U_t^{\mathrm{e}})^\dagger, \quad \text{for } t > t_{\mathrm{M}}. \tag{4.18b}$$

Taking into account both relations, it follows, for $t > t_{\mathrm{M}}$, that

$$\begin{aligned}
\langle W_{\mathrm{ME}\to\mathrm{S}}(t,0)\rangle &= \mathrm{Tr}\left[\rho(H_{\mathrm{S}}(t) - H_{\mathrm{S}}^{\mathrm{s}})\right] \\
&= \mathrm{Tr}\left[\rho(H_{\mathrm{S}}(t) - H_{\mathrm{S}}(t_{\mathrm{M}}) + H_{\mathrm{S}}(t_{\mathrm{M}}) - H_{\mathrm{S}}^{\mathrm{s}})\right] \\
&= \mathrm{Tr}_{\mathrm{SE}}\left[(\rho_{\mathrm{SE}}(t) - \rho_{\mathrm{SE}}(t_{\mathrm{M}}))H_{\mathrm{S}}^{\mathrm{s}}\right] + \mathrm{Tr}_{\mathrm{SE}}\left[(\rho_{\mathrm{SE}}(t_{\mathrm{M}}) - \rho_{\mathrm{SE}})H_{\mathrm{S}}^{\mathrm{s}}\right] \\
&= \mathrm{Tr}_{\mathrm{SE}}\left[(U_t^{\mathrm{e}}\Phi_{A_{\mathrm{S}}}(\rho_{\mathrm{SE}})(U_t^{\mathrm{e}})^\dagger - \Phi_{A_{\mathrm{S}}}(\rho_{\mathrm{SE}}))H_{\mathrm{S}}^{\mathrm{s}}\right] + \\
&+ \mathrm{Tr}_{\mathrm{SE}}\left[(\Phi_{A_{\mathrm{S}}}(\rho_{\mathrm{SE}}) - \rho_{\mathrm{SE}})H_{\mathrm{S}}^{\mathrm{s}}\right].
\end{aligned} \tag{4.19}$$

As per the derivation of (4.14), we can take the term in the last line as the energy disturbance induced by the measurement of A_{S}. In fact, we may as well show that

$$|\,\mathrm{Tr}_{\mathrm{SE}}\left[(\Phi_{A_{\mathrm{S}}}(\rho_{\mathrm{SE}}) - \rho_{\mathrm{SE}})H_{\mathrm{S}}^{\mathrm{s}}\right]\,| \leq \sqrt{2\,\mathcal{I}_{A_{\mathrm{S}}}(\rho_{\mathrm{SE}})}\|H_{\mathrm{S}}^{\mathrm{s}}\|_2. \tag{4.20}$$

Here, contrary to (4.14), $\mathcal{I}_{A_{\mathrm{S}}}(\rho_{\mathrm{SE}})$ cannot be taken just as a measure of coherence on the basis of A_{S}. Indeed, it can be shown [114, 117] that

$$\mathcal{I}_{A_{\mathrm{S}}}(\rho_{\mathrm{SE}}) = \mathcal{I}_{A_{\mathrm{S}}}(\rho_{\mathrm{S}}) + D_{A_{\mathrm{S}}}(\rho_{\mathrm{SE}}), \tag{4.21}$$

where $\mathcal{I}_{A_{\mathrm{S}}}(\rho_{\mathrm{S}})$ relates again to the amount of coherence in the basis of A_{S} and $D_{A_{\mathrm{S}}}(\rho_{\mathrm{SE}}) = I_{\mathrm{S:E}}(\rho) - I_{\mathrm{S:E}}(\Phi_{A_{\mathrm{S}}}(\rho_{\mathrm{SE}}))$ is a discord-like term [114, 117, 135] written in terms of the mutual information $I_{\mathrm{S:E}}(\rho') = S(\rho'||\rho'_{\mathrm{S}} \otimes \rho'_{\mathrm{E}})$. Up to a minimization over all possible observables, $D_{A_{\mathrm{S}}}(\rho_{\mathrm{SE}})$ is the quantum discord, a quantifier of the quantum correlations between S and E. Therefore, in the present case, the local state ρ_{S} may have no coherences with respect to A_{S} and still the measurement may change the energy of the system (if $D_{A_{\mathrm{S}}}(\rho_{\mathrm{SE}}(0)) \neq 0$). We thus see that not only coherences but also quantum correlations between S and E can bound the energy transfer induced by the measurement.

The term $\mathrm{Tr}_{\mathrm{SE}}\left[(U_t^{\mathrm{e}}\Phi_{A_{\mathrm{S}}}(\rho_{\mathrm{SE}})(U_t^{\mathrm{e}})^\dagger - \Phi_{A_{\mathrm{S}}}(\rho_{\mathrm{SE}}))H_{\mathrm{S}}^{\mathrm{s}}\right]$ appearing in the last equality of (4.19) is related to the amount of work that the system E does on S by virtue of the change

[3] We speculate that such a condition could be forced had we added another clock intermediating the interaction between S and E. The assessment of the eventual effects of this clock is left for future work.

$\rho_{\rm SE} \to \Phi_{A_{\rm S}}(\rho_{\rm SE})$ imposed by the measurement. This term shows that the measurement induces energy transfer not only within the interval $[0, t_{\rm M}]$, wherein it is presumed to occur, but also posteriorly. This corresponds to the time interval depicted on the right-hand side of Fig. 4.2(b), where the composite unitary $U_t^{\rm e} = \exp\left[-(i(t-t_{\rm M})/\hbar)H_{\rm SE}\right]$ for the $\rm S+E$ dynamics is governed by the Hamiltonian $H_{\rm SE} = H_{\rm S} + V_{\rm SE} + H_{\rm E}$. Letting[4] $W^{\rm nom}_{\rm E\to S}(t,0) \approx (U_t^{\rm e})^\dagger H_{\rm S}^{\rm s} U_t^{\rm e} - H_{\rm S}^{\rm s}$ be the "no-measurement" work that would have been done on $\rm S$ by $\rm E$ if no measurement had taken place, then we find:

$$\begin{aligned}\langle W_{\rm ME\to S}(t,0)\rangle - \langle W^{\rm nom}_{\rm E\to S}(t,0)\rangle \;&= {\rm Tr}_{\rm SE}\left[(U_t^{\rm e}\Phi_{A_{\rm S}}(\rho_{\rm SE})(U_t^{\rm e})^\dagger - \Phi_{A_{\rm S}}(\rho_{\rm SE}))H_{\rm S}^{\rm s}\right] + \\ &+ {\rm Tr}_{\rm SE}\left[(\Phi_{A_{\rm S}}(\rho_{\rm SE}) - \rho_{\rm SE})H_{\rm S}^{\rm s}\right] + \\ &- {\rm Tr}_{\rm SE}(\rho_{\rm SE}(W^{\rm nom}_{\rm E\to S}(t,0))) \\ &= {\rm Tr}_{\rm SE}\left[(\Phi_{A_{\rm S}}(\rho_{\rm SE}) - \rho_{\rm SE})W^{\rm nom}_{\rm E\to S}(t,0)\right] + \\ &+ {\rm Tr}_{\rm SE}\left[(\Phi_{A_{\rm S}}(\rho_{\rm SE}) - \rho_{\rm SE})H_{\rm S}^{\rm s}\right].\end{aligned} \tag{4.22}$$

With a procedure similar to that employed to derive (4.14) and (4.20), we obtain

$$\frac{|\,\langle W_{\rm ME\to S}(t,0)\rangle - \langle W^{\rm nom}_{\rm E\to S}(t,0)\rangle\,|}{\sqrt{2}} \le \sqrt{\mathcal{I}_{A_{\rm S}}(\rho_{\rm SE})}(\|H_{\rm S}^{\rm s}\|_2 + \|W^{\rm nom}_{\rm E\to S}(t,0)\|_2). \tag{4.23}$$

By comparing a measurement scenario ($\langle W_{\rm ME\to S}(t,0)\rangle$) and a no measurement one ($\langle W^{\rm nom}_{\rm E\to S}(t,0)\rangle$), we highlight two possible effects induced by the measurement: (i) a change of energy during its application, which is associated with the bound $\sqrt{2\,\mathcal{I}_{A_{\rm S}}(\rho_{\rm SE})}\|H_{\rm S}^{\rm s}\|_2$ and (ii) a pertubation in the energy exchange with another system $\rm E$, vinculated with $\sqrt{2\,\mathcal{I}_{A_{\rm S}}(\rho_{\rm SE})}\|W^{\rm non}_{\rm E\to S}(t,0)\|_2$. In both types of disturbance, the role of irreality should not be underestimated: the farther a system is from having an element of reality, the more the measurement can disturb the system; the measurement is not invasive (with respect to energy) when the measured observable is implied by the preparation to be an element of reality. Our result (4.23) corroborates to studies reported in [35, 72], which explore the connection between coherences and correlations with measurement-induced disturbances on the energy balance.

4.4 Take-away messages

In the present chapter, we formalized minimal conditions that protocols measuring variations of energy are expected to satisfy in order to preserve the law of conservation of energy. The analysis is conducted in terms of probabilities so that no specific instrument or concrete protocol is considered *a priori*. We demonstrated that the two-time quantum observable view defended in the previous chapter not only satisfy these minimal conditions,

[4] Here we considered the fact that, due to Hypotheses 2, in the no-measurement scenario it follows that $U_{t_{\rm M}}^\dagger H_{\rm S}^{\rm s} U_{t_{\rm M}} \approx H_{\rm S}^{\rm s}$, where $U_{t_{\rm M}} = \exp\left[-(i(t_{\rm M})/\hbar)H_{\rm SE}\right]$. As a result, $W^{\rm nom}_{\rm E\to S}(t,0) = (U_t^{\rm e})^\dagger U_{t_{\rm M}}^\dagger H_{\rm S}^{\rm s} U_{t_{\rm M}} U_t^{\rm e} - H_{\rm S}^{\rm s} \approx (U_t^{\rm e})^\dagger H_{\rm S}^{\rm s} U_t^{\rm e} - H_{\rm S}^{\rm s}$.

but also satisfy stronger conservation requirements. Moreover, we demonstrate how the law of conservation of energy emerges naturally as an EPR element of reality in the quantum realm once we adopt a two-time quantum observable perspective.

In Section 4.3, we showed how we can include the measurement in order to compute its energetic disturbances on the measured system and deduced a bound for such disturbances. It turns out that BA measure of irreality, accounting for the fundamental undefiniteness of the measured observable, limits how much the measurement disturbs energetically a given system. Moreover, the disruptive nature of the measurement was shown to affect also energy exchanges taking place at posterior time intervals, with further systems. Finally, we identified the roles of coherences and quantum correlations (as encoded in the preparation) in restricting the energy disturbance introduced by measurements.

5 QM work: features and perspectives

Before approaching scenarios closer to thermodynamics, we show in the present chapter many interesting mathematical results deduced as direct consequences of treating work as a two-time quantum observable. Although we could not thoroughly investigate the main physical implications of these mathematical results, we expect them to be considered as starting points for more profound studies in the future. We thus outlined some possible research directions throughout the text.

5.1 A corresponding Schrödinger operator

We consider once again a universe U initially prepared in a state ρ acting on the Hilbert space $\mathbb{H} = \mathbb{H}_{\mathrm{S}} \otimes \mathbb{H}_{\mathrm{E}}$, whose dynamics is described by the autonomous Hamiltonian operator

$$H = H_{\mathrm{S}} + V_{\mathrm{SE}} + H_{\mathrm{E}}, \tag{5.1}$$

where S is the system of interest and E an environment interacting with S. Again, E may be any other system (including a measurement apparatus), with no particular restriction. Given this configuration, our aim is to show that we can always identify a Schrödinger observable that commutes with work. Therefore, with the prescription for obtaining work statistics in Chapter 3, we can raise the statistics of work from measurements of this Schrödinger operator.

In usual contexts of quantum mechanics, the Baker-Hausdorf (BH) [103] relation can be considered, which, when applied on the Heisenberg energy operator $H_{\mathrm{S}}(t)$ evolved accordingly with the unitary $U(t) = U_t = \exp\left[-iHt/\hbar\right]$, gives

$$H_{\mathrm{S}}(t) = U_t^{\dagger} H_{\mathrm{S}}^{\mathrm{s}} U_t = \sum_{n=1}^{\infty} \left(\frac{t}{i\hbar}\right)^n \left([\cdot, H]\right)^n H_{\mathrm{S}}^{\mathrm{s}}, \tag{5.2}$$

where $\left([\cdot, H]\right) A = [A, H]$ and $\left([\cdot, H]\right)^k A = \left([\cdot, H]\right)^{k-1} [A, H]$ for any natural $k \geq 1$ and operator A. The terms $\left([\cdot, H]\right)^n H_{\mathrm{S}}^{\mathrm{s}}$ are expected to be written in terms of product or sums of Schrödinger operators, whose result is also a Schrödinger operator. In this sense, when we fix a real valued time $t = t_1$, we have that

$$H_{\mathrm{S}}(t_1) = \sum_{n=1}^{\infty} c_n C_n^{\mathrm{s}} \tag{5.3}$$

where $c_n = \left(t_1/(i\hbar)\right)^n$ are just complex values and $C_n^{\mathrm{s}} = \left([\cdot, H]\right)^n H_{\mathrm{S}}^{\mathrm{s}}$ are Schrödinger operators written in terms of other Schrödinger operators. Therefore, by fixing a time t_1 for $H_{\mathrm{S}}(t)$, we can always identify a Schrödinger operator resulting from a weighted sum of other Schrödinger operators. The same procedure can be adopted when we specify another time

t_2, thus yielding a Heisenberg operator $H_{\rm S}(t_2) = \sum_{n=1}^{\infty} d_n C_n^{\rm s}$. Notice that $\{C_n^{\rm s}\}$ may act on the role universe U Hilbert space, as explicitly shown in Subsection 3.2.2. With t_1 and t_2 specified, we then obtain another Schrödinger operator

$$B^{\rm s} = \sum_{n=1}^{\infty} (d_n - c_n) C_n^{\rm s} \tag{5.4}$$

which should be equal to $W_{\rm E\to S}(t_2, t_1) = H_{\rm S}(t_2) - H_{\rm S}(t_1)$ for the very specific fixed times $t_{1,2}$. Therefore, by fixing arbitrary intervals $[t_1, t_2]$ and using the procedure prescribed above, we can always find a Schrödinger operator which equals $W_{\rm E\to S}(t_2, t_1) = H_{\rm S}(t_2) - H_{\rm S}(t_1)$. Indeed, the formalism here is in no way restricted to the form of the operators, so that it is general as long as the BH formula is valid.

5.2 Energy eigenbasis and equilibration

How difficult is to diagonalize or even describe the work operator and its basis? As the most well-known methods of diagonalization are constructed for the energy operators, it seems that a whole new formalim must be conceived for work operator. Fortunately, we show in the present section that we can construct the work operator by means of the energy basis, so that not necessarily a new method must be developed for work operators.

We consider the same bipartide system formalized in (5.1). Since $W_{\rm E\to S}(t_2, t_1) = H_{\rm S}(t_2) - H_{\rm S}(t_1) = U_{t_2}^{\dagger} H_{\rm S}^{\rm s} U_{t_2} - U_{t_1}^{\dagger} H_{\rm S}^{\rm s} U_{t_1}$, then we can use the total energy basis $\{|e_i\rangle\}$, satisfying $H|e_i\rangle = e_i|e_i\rangle$, to write

$$\begin{aligned} \langle e_i| W_{\rm E\to S}(t_2, t_1) |e_j\rangle &= \langle e_i| \left(U_{t_2}^{\dagger} H_{\rm S}^{\rm s} U_{t_2} - U_{t_1}^{\dagger} H_{\rm S}^{\rm s} U_{t_1}\right) |e_j\rangle \\ &= \left[{\rm e}^{-\frac{i(e_j - e_i)(\Delta t)}{\hbar}} - 1 \right] {\rm e}^{\frac{ie_i t_1}{\hbar}} \langle e_i| H_{\rm S}^{\rm s} |e_j\rangle , \end{aligned} \tag{5.5}$$

where $\Delta t = t_2 - t_1$. Therefore, by identifying the energy basis and determining $\langle e_i| H_{\rm S}^{\rm s} |e_j\rangle$, one is able to construct the work operator in terms of the energy basis as in Eq. (5.5). Given the matrix elements $\langle e_i| W_{\rm E\to S}(t_2, t_1) |e_j\rangle$, work eigenbasis can be determined with standard methods of linear algebra in quantum mechanics.

Interestingly, Eq.(5.5) can be considered in connection with equilibration scenarios. It is a known fact [136–138] that for sufficiently long time a system tends to equilibrate, approaching a certain type of thermodynamics equilibrium. An evidence of that is found by use of the time-averaged state

$$\overline{\rho} \equiv \frac{1}{T'} \int_0^{T'} dt\ U_t \rho U_t^{\dagger}. \tag{5.6}$$

We can check that in the limit in which $T' \to \infty$ $\overline{\rho} \to \Phi_H(\rho)$, i.e. all the energy coherences of ρ vanish meaning that energy becomes a BA element of reality. This result can be interpreted as follows: given that equilibrium thermodynamics time scales are much bigger than that of the microscopic interactions, then the events that appears to be instantaneous

in a thermodynamics scale actually occurs during a window of time $[0, T]$ which is big in a microscopic scale [104, 139]. Therefore, in thermodynamics limit applications, we are usually able to access time average properties of large macroscopic systems and not their "frozen" quantities at a specific given time. The state $\overline{\rho}$ is therefore the state that describes this average properties and it is related to the thermalization of the system. In fact, we can also compute a time average QM work as:

$$\overline{\langle W_{\mathrm{E}\to\mathrm{S}}(t_1+\Delta T, t_1)\rangle} = \frac{1}{\Delta T}\int_0^{\Delta T} \langle W_{\mathrm{E}\to\mathrm{S}}(t_1+\Delta t, t_1)\rangle \, d(\Delta t). \tag{5.7}$$

Considering (5.5), we can write

$$\begin{aligned}\langle W_{\mathrm{E}\to\mathrm{S}}(t_1+\Delta T, t_1)\rangle &= \mathrm{Tr}\left[\rho W_{\mathrm{E}\to\mathrm{S}}(t_1+\Delta t, t_1)\right] = \textstyle\sum_{i,j} \langle e_j|\,\rho\,|e_i\rangle \langle e_i|\, W_{\mathrm{E}\to\mathrm{S}}(t_1+\Delta t, t_1)\,|e_j\rangle \\ &= \textstyle\sum_{i,j} \langle e_j|\,\rho\,|e_i\rangle \left[\mathrm{e}^{-\frac{i(e_j-e_i)(\Delta t)}{\hbar}} - 1\right] \mathrm{e}^{\frac{ie_i t_1}{\hbar}} \langle e_i|\, H_{\mathrm{S}}\,|e_j\rangle\end{aligned} \tag{5.8}$$

so that, for a sufficiently long interval ΔT, we have

$$\overline{\langle W_{\mathrm{E}\to\mathrm{S}}(t_1+\Delta t, t_1)\rangle} = \lim_{\Delta T\to\infty} \frac{1}{\Delta T}\int_0^{\Delta T} \mathrm{Tr}\left[\rho W_{\mathrm{E}\to\mathrm{S}}(t_1+\Delta t, t_1)\right] d(\Delta t) = 0. \tag{5.9}$$

As a result, the time-averaged mean work will be null for a sufficiently long time. We can consider the same interpretation as before: if $W_{\mathrm{E}\to\mathrm{S}}(t_1+\Delta t, t_1)$ is related to microscopic interactions with very short time-scales, then no work is averagely observed within a characteristic interval of equilibrium thermodynamics. As a consequence, the amount of energy that flows into the system eventually goes out and vice-versa. On the other hand, if $W_{\mathrm{E}\to\mathrm{S}}(t_1+\Delta t, t_1)$ can be related to a macroscopic degree of freedom with large time-scales, then the assumption $\Delta T \to \infty$ implies that the interval must be extremely large for work to be null.

5.3 What if the energies commute?

Let us assume that for the instants of time t_1' and t_2', $[H_{\mathrm{S}}(t_1'), H_{\mathrm{S}}(t_2')] = 0$. It follows immediately from this assumption that

$$[W_{\mathrm{E}\to\mathrm{S}}(t_2', t_1'), H_{\mathrm{S}}(t_1')] = [W_{\mathrm{E}\to\mathrm{S}}(t_2', t_1'), H_{\mathrm{S}}(t_2')] = 0. \tag{5.10}$$

Now, given a general (autonomous) unitary evolution U_t, we can deduce, for arbitrary instants t, t', t'', the following properties: (i) $U_t^\dagger H_{\mathrm{S}}(t') U_t = H_{\mathrm{S}}(t'+t)$ and (ii) $U_t^\dagger [H_{\mathrm{S}}(t'), H_{\mathrm{S}}(t'')] U_t = [U_t^\dagger H_{\mathrm{S}}(t') U_t, U_t^\dagger H_{\mathrm{S}}(t'') U_t] = [H_{\mathrm{S}}(t'+t), H_{\mathrm{S}}(t''+t)]$. With these properties in mind and with the assumption $[H_{\mathrm{S}}(t_1'), H_{\mathrm{S}}(t_2')] = 0$, we can compute the following results:

$$\begin{aligned}[H_{\mathrm{S}}(t_1'), H_{\mathrm{S}}(t_2')] = 0 \quad &\Longrightarrow\quad U_{t_1'}[H_{\mathrm{S}}(t_1'), H_{\mathrm{S}}(t_2')] U_{t_1}^\dagger = 0 \\ &\Longrightarrow\quad [H_{\mathrm{S}}^{\mathrm{s}}, H_{\mathrm{S}}(t_2'-t_1')] = 0 \\ &\Longrightarrow\quad U_t^\dagger [H_{\mathrm{S}}^{\mathrm{s}}, H_{\mathrm{S}}(t_2'-t_1')] U_t = 0 \\ &\Longrightarrow\quad [H_{\mathrm{S}}(t), H_{\mathrm{S}}(t+t_2'-t_1')] = 0,\end{aligned} \tag{5.11}$$

Therefore, for intervals $[t, t+\Delta t']$ of the same time-length $\Delta t' = t_2' - t_1'$, one has

$$[W_{\mathrm{E}\to\mathrm{S}}(\Delta t + t, t), H_{\mathrm{S}}(t)] = [W_{\mathrm{E}\to\mathrm{S}}(\Delta t + t, t), H_{\mathrm{S}}(\Delta t + t)] = 0. \tag{5.12}$$

Therefore, if one finds out an interval Δt in which both energies operators commute, then instantaneously, one find out infinite other time-intervals of the same length for which the energies commute. As a result, if one prepares a state such in which the energy of the system at a time t is completely determined, then the work during the intervals $[t, t+\Delta t]$ and $[t-\Delta t, t]$ are automatically known.

Interestingly, we can also show that work and H share the same eigenbasis if and only if $W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1) = 0$; in other words, $[W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1), H] = 0 \iff W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1) = 0$. To prove this, let us suppose first the contradiction:

$$[W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1), H] = 0 \tag{5.13}$$

and $W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1) = H_{\mathrm{S}}(t_2) - H_{\mathrm{S}}(t_1) \neq 0$. Given that H is nondegenerate, Eq. (5.13) then implies that the eigenvectors $\{|e_j\rangle\}$ that diagonalizes H also diagonalizes $W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1)$. For $W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1)$ to be different from the null operator there must be at least an eigenvector $|e_j\rangle$ such that $W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1)|e_j\rangle = w_j|e_j\rangle$, with $w_j \neq 0$. Therefore, for this specific $|e_j\rangle$, we have $\langle e_j| W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1)|e_j\rangle = w_j \neq 0$. However, it is straightforwardly deduced from (5.5) that $\langle e_j| W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1)|e_j\rangle = 0$, which is clearly a contradiction. Therefore, $[W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1), H] = 0 \implies W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1) = 0$ and conversely, it is obvious that $W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1) = 0 \implies [W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1), H] = 0$, so that $[W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1), H] = 0 \iff W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1) = 0$. An interesting physical implication of this result is that if we find out two times $t_{1,2}$ in which the power are exactly the negative of each other, so that $[H_{\mathrm{S}}(t_1), H]/i\hbar = -[H_{\mathrm{S}}(t_2), H]/i\hbar \implies [H_{\mathrm{S}}(t_2) - H_{\mathrm{S}}(t_1), H] = 0$, then it follows that work is exactly null in that interval $W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1) = 0$. Moreover, from a computation similar to (5.11), $W_{\mathrm{E}\to\mathrm{S}}(t_2 - t_1 + t, t) = 0$ for any t.

5.4 Work, time, and fluctuations of energy

We show now that for a given amount of work to be transferred in a fast way to a system S, then a raise in the fluctuations of energy must be induced. To prove this result, we first notice that $W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1) = H_{\mathrm{S}}(t_2) - H_{\mathrm{S}}(t_1) = \int_{t_1}^{t_2} \dot{H}_{\mathrm{S}}(t)dt$, where the Heisenberg equation gives us $\dot{H}_{\mathrm{S}}(t) = [H_{\mathrm{S}}(t), H]/(i\hbar)$. Now, considering the Heisenberg uncertainty relation $|\langle [H_{\mathrm{S}}(t), H]\rangle|/2 \leq \sigma_{H_{\mathrm{S}}(t)}\sigma_H$, we get

$$|\langle W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1)\rangle| = \left|\int_{t_1}^{t_2} \dot{H}_{\mathrm{S}}(t)dt\right| \leq \int_{t_1}^{t_2} \left|\dot{H}_{\mathrm{S}}(t)\right| dt \leq \frac{2}{\hbar}\sigma_H \int_{t_1}^{t_2} \sigma_{H_{\mathrm{S}}(t)}dt \tag{5.14}$$

By defining $\sigma_{H_{\mathrm{S}}}^{\max} = \max_{t\in[t_1,t_2]} \sigma_{H_{\mathrm{S}}(t)}$, we find

$$\frac{|\langle W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1)\rangle|}{2\sigma_{H_{\mathrm{S}}}^{\max}\Delta t} \leq \frac{2\sigma_H}{\hbar}. \tag{5.15}$$

As a result, we have a trade-off between the average work $\langle W_{\mathrm{E}\to\mathrm{S}}(t_2,t_1)\rangle$ that can be done on S, the time Δt intended for this amount of energy to be transferred, and the local fluctuations of energies $\sigma^{\max}_{H_\mathrm{S}}$. In summary, the time average power $\langle W_{\mathrm{E}\to\mathrm{S}}(t_2,t_1)\rangle/\Delta t$ is bounded by energy fluctuations.

Interestingly, fast processes in thermodynamics are frequently related to dissipative phenomena. A compelling line of research would be the investigation of the connection between the result (5.15) and such phenomena. Perhaps, some results in the literature of Thermodynamics Uncertain Relations (TURs) [140, 141] may guide such research.

5.5 Bounds on QM work

In the present section, we aim at studying bounds on the QM work without necessarily resorting to thermodynamics ingredients. To avoid excessive notation, in this section we will denote $W_{\mathrm{E}\to\mathrm{S}}(t,0)$ simply as W. Using this notation, we first show that:

$$\langle \mathrm{e}^{-\nu W}\rangle \geq \mathrm{e}^{-\nu\langle W\rangle} \geq \mathrm{e}^{-S(\rho(t)||\rho_\nu)}. \tag{5.16}$$

where $\rho(t) = U_t\rho U_t^\dagger$, ν is a non-negative real value, $S(\rho(t)||\rho_\nu)$ again denotes the quantum relative entropy, and

$$\rho_\nu := \frac{\mathrm{e}^{-\nu H_\mathrm{S}^\mathfrak{s}}}{\mathcal{Z}^\nu_{H_\mathrm{S}}}, \quad \mathcal{Z}^\nu_{H_\mathrm{S}} = \mathrm{Tr}\left[\mathrm{e}^{-\nu H_\mathrm{S}^\mathfrak{s}}\right]. \tag{5.17}$$

Proof. We deduced in the Appendix B for any quantum observable $A^\mathfrak{s}$ acting on $\mathbb{H} = \mathbb{H}_\mathrm{S}\otimes\mathbb{H}_\mathrm{E}$ and real non-negative values ν and[1] $T_\nu = (k_\mathrm{B}\nu)^{-1}$ that:

$$F_A(\rho) := \langle A\rangle - k_\mathrm{B}T_\nu S(\rho) \geq -k_\mathrm{B}T_\nu \ln \mathcal{Z}^\nu_A \implies \nu(\langle A\rangle - k_\mathrm{B}T_\nu S(\rho)) \geq -\ln \mathcal{Z}^\nu_A, \tag{5.18}$$

where $S(\rho) = -\mathrm{Tr}\,(\rho\ln\rho)$ is the von Neumann entropy and $\mathcal{Z}^\nu_A = \mathrm{Tr}\left[\mathrm{e}^{-\nu A^\mathfrak{s}}\right]$. Since $x\geq y \implies \mathrm{e}^x \geq \mathrm{e}^y$, then

$$\mathrm{e}^{\nu(\langle A\rangle - k_\mathrm{B}T_\nu S(\rho))} \geq (\mathcal{Z}^\nu_A)^{-1} \implies \mathcal{Z}^\nu_A \geq \mathrm{e}^{-\nu(\langle A\rangle - k_\mathrm{B}T_\nu S(\rho))}. \tag{5.19}$$

With the substitution $A^\mathfrak{s}\to H_\mathrm{S}^\mathfrak{s}$, we obtain

$$\mathcal{Z}^\nu_{H_\mathrm{S}} \geq \mathrm{e}^{-\nu(\langle H_\mathrm{S}(0)\rangle - k_\mathrm{B}T_\nu S(\rho))}. \tag{5.20}$$

Taking (5.17) into account and the fact that $S(\rho(t)) = S(U_t\rho U_t^\dagger) = S(\rho)$, we compute the following relation:

$$\begin{aligned} k_\mathrm{B}S(\rho(t)||\rho_\nu) &= -k_\mathrm{B}\,\mathrm{Tr}\left[\rho(t)\ln\rho_\nu\right] - k_\mathrm{B}S(\rho(t)) \\ &= -k_\mathrm{B}\,\mathrm{Tr}\left[\rho(t)\ln\rho_\nu\right] - k_\mathrm{B}S(\rho) \\ &= k_\mathrm{B}\nu\,\mathrm{Tr}(\rho(t)H_\mathrm{S}^\mathfrak{s}) + k_\mathrm{B}\ln\mathcal{Z}^\nu_{H_\mathrm{S}} - k_\mathrm{B}S(\rho) \\ &= k_\mathrm{B}\nu\,\langle H_\mathrm{S}(t)\rangle + k_\mathrm{B}\ln\mathcal{Z}^\nu_{H_\mathrm{S}} - k_\mathrm{B}S(\rho). \end{aligned} \tag{5.21}$$

[1] In the Appendix, we did not consider the Boltzmann constant k_B in the relation between T_ν and ν. Here, we considered k_B aiming at a connection between our results and usual thermodynamics ones.

Therefore,

$$\mathrm{e}^{\nu(k_\mathrm{B}T_\nu S(\rho(t)||\rho_\nu))} = \mathrm{e}^{-\nu(-\langle H_\mathrm{S}(t)\rangle - k_\mathrm{B}T_\nu \ln \mathcal{Z}^\nu_{H_\mathrm{S}} + k_\mathrm{B}T_\nu S(\rho))} \tag{5.22}$$

Multiplying both sides of inequality (5.20) by $\mathrm{e}^{\nu(k_\mathrm{B}T_\nu S(\rho(t)||\rho_\nu))}$ and considering (5.22), we get

$$\mathrm{e}^{\nu(k_\mathrm{B}T_\nu S(\rho(t)||\rho_\nu))}\mathcal{Z}^\nu_{H_\mathrm{S}} \geq \mathrm{e}^{-\nu(-\langle H_\mathrm{S}(t)\rangle + \langle H_\mathrm{S}(0)\rangle - k_\mathrm{B}T_\nu \ln \mathcal{Z}^\nu_{H_\mathrm{S}} + k_\mathrm{B}T_\nu S(\rho) - k_\mathrm{B}T_\nu S(\rho))}. \tag{5.23}$$

Rearranging the terms with $\langle W\rangle = \langle H_\mathrm{S}(t)\rangle - \langle H_\mathrm{S}(0)\rangle$ and using Jensen's inequality for the exponential $\langle \mathrm{e}^x\rangle \geq \mathrm{e}^{\langle x\rangle}$, we get (5.16). □

For any non-negative scalar ν and any state ρ, relation (5.16) therefore imposes a limit to $\langle \mathrm{e}^{-\nu W}\rangle$ without in any way resorting to thermodynamics ingredients, although with algebraic similarities. Indeed, although ρ_ν has form similar to a canonical state $\mathrm{e}^{-\beta H}/\mathcal{Z}$, it must not be interpreted as so, since ν is an arbitrary real value not necessarily related to an inverse temperature β. Interestingly, H^s_S can be written as $H^\mathrm{s}_\mathrm{S} \equiv (H^\mathrm{s}_\mathrm{S})_\mathrm{L} \otimes \mathbb{1}_\mathrm{E}$ in terms of the local energy operator $(H^\mathrm{s}_\mathrm{S})_\mathrm{L}$ (that acts only on $\mathbb{H}_\mathrm{S}$) so that we can rewrite ρ_ν as

$$\rho_\nu = \frac{\mathrm{e}^{-\nu H^\mathrm{s}_\mathrm{S}}}{\mathcal{Z}^\nu_{H_\mathrm{S}}} \equiv \frac{\mathrm{e}^{-\nu (H^\mathrm{s}_\mathrm{S})_\mathrm{L}\otimes \mathbb{1}_\mathrm{E}}}{\mathcal{Z}^\nu_{H_\mathrm{S}}} = \frac{\mathrm{e}^{-\nu (H^\mathrm{s}_\mathrm{S})_\mathrm{L}}}{\mathcal{Z}'^\nu_{H_\mathrm{S}}} \otimes \frac{\mathbb{1}}{d_\mathrm{E}}, \quad \mathcal{Z}'^\nu_{H_\mathrm{S}} = \mathrm{Tr}_\mathrm{S}\left[\mathrm{e}^{-\nu (H^\mathrm{s}_\mathrm{S})_\mathrm{L}}\right], \tag{5.24}$$

where d_E is the dimension of the Hilbert space $\mathbb{H}_\mathrm{E}$. Therefore, in the special case in which ν can be associated with an inverse temperature β, then ρ_ν can be interpreted as a local canonical state for S and a perfect mixture for E.

Now, considering the fact that $\mathcal{Z}^\nu_{H_\mathrm{S}} = \mathrm{Tr}\left[\mathrm{e}^{-\nu H^\mathrm{s}_\mathrm{S}}\right] = \mathrm{Tr}\left[U_t^\dagger \mathrm{e}^{-\nu H^\mathrm{s}_\mathrm{S}} U_t\right] = \mathrm{Tr}\left[\mathrm{e}^{-\nu H_\mathrm{S}(t)}\right] = \mathcal{Z}^\nu_{H_\mathrm{S}(t)}$ then we can show from (5.18), that

$$\mathcal{Z}^\nu_{H_\mathrm{S}} \geq \mathrm{e}^{-\nu(\langle H_\mathrm{S}(t)\rangle - k_\mathrm{B}T_\nu S(\rho))}, \tag{5.25}$$

and, by using a similar procedure as in the proof above, we can show that

$$\mathrm{e}^{S(\rho||\rho_\nu)} \geq \mathrm{e}^{-\nu\langle W\rangle}. \tag{5.26}$$

As a result, we can deduce that

$$\mathrm{e}^{S(\rho||\rho_\nu)} \geq \mathrm{e}^{-\nu\langle W\rangle} \geq \mathrm{e}^{-S(\rho(t)||\rho_\nu)}, \tag{5.27}$$

which, taking into account that $\nu = (k_\mathrm{B}T_\nu)^{-1}$, also leads to

$$k_\mathrm{B}T_\nu S(\rho(t)||\rho_\nu) \geq \langle W\rangle \geq -k_\mathrm{B}T_\nu S(\rho||\rho_\nu). \tag{5.28}$$

Therefore, we have a limit for the energy that can be extracted from S, $-\langle W\rangle \leq k_\mathrm{B}T_\nu S(\rho||\rho_\nu)$, and a maximal amount of work that can be done on S, namely, $\langle W\rangle \leq T_\nu S(\rho(t)||\rho_\nu)$. Notably, since the inequality is valid for any ν, if the state has an initial form ρ_ν, then no energy can be extracted from S; similarly, if the state ends up in ρ_ν, with any ν, then the work done cannot be greater than 0.

We emphasize that Eq. (5.28) does not contradict the bounds shown in Section 2.6, since we are concerned here with QM work, instead of a thermodynamics notion of work. Nevertheless, an interesting line of research would be the detailed investigation of the connection between the bounds on QM work deduced here and those of thermodynamics.

5.5.1 Minimum relative entropy

Since relations (5.27) and (5.28) are valid for any ν, then we may consider the ν that restrict them at most. To obtain the most restrictive scenario, let us minimize $k_{\rm B}T_\nu S(\rho||\rho_\nu) = (1/\nu)S(\rho||\rho_\nu)$, in terms of ν. In this direction, we first notice that, for fixed ρ, $(1/\nu)S(\rho||\rho_\nu)$ can be seen as a function of ν. We can thus derive $(1/\nu)S(\rho||\rho_\nu)$ with respect to ν and equate it to 0, so as to find the necessary condition for the minimum value of $(1/\nu)S(\rho||\rho_\nu)$ in terms of ν. Since

$$\begin{aligned}\partial_\nu\left[\tfrac{1}{\nu}S(\rho||\rho_\nu)\right] &= -\tfrac{1}{\nu^2}S(\rho||\rho_\nu)+\tfrac{1}{\nu}\partial_\nu S(\rho||\rho_\nu)\\ &= -\tfrac{1}{\nu^2}S(\rho||\rho_\nu)+\tfrac{1}{\nu}\left(\langle H_{\rm S}(0)\rangle+\partial_\nu\ln\mathcal{Z}\right)\\ &= -\tfrac{1}{\nu^2}S(\rho||\rho_\nu)+\tfrac{1}{\nu}\left(\langle H_{\rm S}(0)\rangle-\langle H_{\rm S}\rangle_\nu\right),\end{aligned} \tag{5.29}$$

where we denoted $\langle H_{\rm S}(0)\rangle_\nu = {\rm Tr}\left[\rho_\nu H_{\rm S}^{\rm s}\right]$, then

$$\partial_\nu\frac{1}{\nu}S(\rho||\rho_\nu)=0 \iff TS(\rho||\rho_\nu)=\langle H_{\rm S}(0)\rangle-\langle H_{\rm S}\rangle_\nu\,. \tag{5.30}$$

Notice that in the case in which $\rho=\rho_\nu$, then (5.30) is trivially satisfied. Now, to confirm that the condition (5.30) really gives a minimum (and not a maximal or saddle point [142]), we notice that the second-derivative is non-negative at the point ν^* which satisfies (5.30):

$$\partial_\nu^2\left[\frac{1}{\nu}S(\rho||\rho_{\nu^*})\right]=\frac{\langle H_{\rm S}^2\rangle_{\nu^*}}{\nu^*}\geq 0 \tag{5.31}$$

As a result, the parameter ν^* that satisfies

$$k_{\rm B}T_\nu S(\rho||\rho_{\nu^*})=\langle H_{\rm S}(0)\rangle-\langle H_{\rm S}\rangle_{\nu^*}\,, \tag{5.32}$$

if it exists, is a minimum of the function $k_{\rm B}T_\nu S(\rho||\rho_\nu)$. Similarly, we can deduce that if exists a parameter ν' satisfying

$$k_{\rm B}T_{\nu'}S(\rho(t)||\rho_{\nu'})=\langle H_{\rm S}(t)\rangle-\langle H_{\rm S}\rangle_{\nu'}\,, \tag{5.33}$$

then this point is the minimal of $k_{\rm B}T_\nu S(\rho(t)||\rho_\nu)$. Assuming that there exist parameters ν^* and ν' that satisfy (5.32) and (5.33), then it follows that

$$-\min_\nu\left[\frac{1}{\nu}S(\rho(t)||\rho_\nu)\right]\leq\langle W\rangle\leq\min_\nu\left[\frac{1}{\nu}S(\rho(t)||\rho_\nu)\right] \tag{5.34}$$

and

$$\langle H_{\rm S}\rangle_{\nu^*}-\langle H_{\rm S}(0)\rangle\leq\langle W\rangle\leq\langle H_{\rm S}(t)\rangle-\langle H_{\rm S}\rangle_{\nu'}\,. \tag{5.35}$$

Moreover, since $S(\rho(t))=S(\rho)$, we can deduce for any non-negative ν that

$$k_{\rm B}T_\nu S(\rho(t)||\rho_\nu)=\langle H_{\rm S}(t)\rangle+k_{\rm B}T_\nu\ln\mathcal{Z}_{H_{\rm S}}^\nu-k_{\rm B}T_\nu S(\rho(t)), \tag{5.36}$$

which, together with the minimum condition (5.33), implies that

$$\langle H_{\rm S}(t)\rangle + k_{\rm B}T_{\nu'}\ln \mathcal{Z}_{H_{\rm S}}^{\nu'} - k_{\rm B}T_{\nu'}S(\rho(t)) = \langle H_{\rm S}(t)\rangle - \langle H_{\rm S}\rangle_{\nu'}\,, \tag{5.37}$$

so that

$$k_{\rm B}T_{\nu'}\ln \mathcal{Z}_{H_{\rm S}}^{\nu'} - k_{\rm B}T_{\nu'}S(\rho(t)) = -\langle H_{\rm S}\rangle_{\nu'}\,. \tag{5.38}$$

But since, for any ν, $k_{\rm B}T_{\nu}S(\rho_{\nu}) = k_{\rm B}T_{\nu}\ln \mathcal{Z}_{H_{\rm S}}^{\nu} + \langle H_{\rm S}\rangle_{\nu}$, then, from (5.38), we deduce that

$$S(\rho) = S(\rho_{\nu'}). \tag{5.39}$$

Therefore, a parameter ν' minimizes $S(\rho(t)||\rho_{\nu})$ if and only if the relations (5.33) and (5.39) follow. Consequently, if for a given evolved state $\rho(t)$ there is a parameter ν', such that $S(\rho) = S(\rho_{\nu'})$, then this parameter will not only minimize $S(\rho(t)||\rho_{\nu})$ but also will be related to the maximum work $\langle H_{\rm S}(t)\rangle - \langle H_{\rm S}\rangle_{\nu'}$ that can be done on the system. Similarly, an analogous relation can be deduced for the lower bound in (5.34), regarding the minimum condition (5.32): in this case, ν^* minimizes $S(\rho||\rho_{\nu})$ if and only if the relations (5.32) and

$$S(\rho) = S(\rho_{\nu^*}) \tag{5.40}$$

are valid. As a result, one may find the maximum value of energy extracted from S, $\langle H_{\rm S}\rangle_{\nu^*} - \langle H_{\rm S}(0)\rangle$. Notice that not always we will find out such ν^* or ν'. For instance, if ρ is a pure state, than since $S(\rho_{\nu}) \geq \ln d_{\rm E}$ for any ν, then there is no ν with the same entropy of ρ, so that there is no ν that satisfies the condition (5.40).

All these results allow for a possible geometrical interpretation of the bounds on QM work. Regarding the upper bound condition in (5.34) in which $\nu = \nu'$, and considering (5.39), we have

$$\begin{aligned}\langle W\rangle \leq k_{\rm B}T_{\nu'}S(\rho(t)||\rho_{\nu'}) &= -k_{\rm B}T_{\nu'}(\mathrm{Tr}\,\rho(t)(\ln\rho_{\nu'}) - S(\rho(t)))\\ &= -k_{\rm B}T_{\nu'}(\mathrm{Tr}\,\rho(t)(\ln\rho_{\nu'}) - S(\rho_{\nu'}))\\ &= -k_{\rm B}[T_{\nu'}\,\mathrm{Tr}(\rho(t) - \rho_{\nu'})(\ln\rho_{\nu'}).\end{aligned} \tag{5.41}$$

Now, using the fact that $\ln\rho_{\nu} = -\nu H_{\rm S} - \ln \mathcal{Z}_{H_{\rm S}}^{\nu}$ and from Cauchy-Schwartz inequality, then we find

$$\langle W\rangle \leq k_{\rm B}T_{\nu}S(\rho(t)||\rho_{\nu'}) \leq \|\rho(t) - \rho_{\nu'}\|_2\|H_{\rm S}\|_2. \tag{5.42}$$

We now show that this also imply that

$$\langle W\rangle \leq \min_{\nu}\{\|\rho(t) - \rho_{\nu}\|_2\}\,\|H_{\rm S}\|_2. \tag{5.43}$$

Proof. To prove this bound, we first notice that if ν' minimizes $\|\rho(t) - \rho_{\nu}\|_2$, then the result follows directly from (5.42). On the other hand, suppose that there is a $\nu'' \neq \nu'$, that minimizes $\|\rho - \rho_{\nu}\|_2$ and also that the inequality is not valid, i.e. $\langle W\rangle > \min_{\nu}\{\|\rho(t) - \rho_{\nu}\|_2\}\,\|H_{\rm S}\|_2 = \|\rho(t) - \rho_{\nu''}\|_2\|H_{\rm S}\|_2$. If this is true, then it follows that

$$\begin{aligned}\|\rho(t) - \rho_{\nu'}\|_2\|H_{\rm S}\|_2 &\geq k_{\rm B}T_{\nu'}S(\rho(t)||\rho_{\nu'})\\ &\geq \langle W\rangle > \|\rho(t) - \rho_{\nu''}\|_2\|H_{\rm S}\|_2 \geq k_{\rm B}T_{\nu''}S(\rho(t)||\rho_{\nu''})\end{aligned} \tag{5.44}$$

so that $k_{\mathrm{B}}T_{\nu'}S(\rho(t)||\rho_{\nu'}) \geq k_{\mathrm{B}}T_{\nu''}S(\rho(t)||\rho_{\nu''})$, which contradicts the fact that $k_{\mathrm{B}}T_{\nu}S(\rho(t)||\rho_{\nu'})$ is the minimum value for $TS(\rho(t)||\rho_{\nu})$. Therefore, there can be no such situation in which $\langle W\rangle > \min_{\nu}\left\{\|\rho(t)-\rho_{\nu}\|_2\right\}\|H_{\mathrm{S}}\|_2$. □

A similar proof can be considered for the lower bound of (5.34), so that we can deduce that

$$-\min_{\nu}\left\{\|\rho-\rho_{\nu}\|_2\right\}\|H_{\mathrm{S}}\|_2 \leq \langle W\rangle \leq \min_{\nu}\left\{\|\rho(t)-\rho_{\nu}\|_2\right\}\|H_{\mathrm{S}}\|_2. \tag{5.45}$$

If the operator $H_{\mathrm{S}}^{\mathrm{s}}$ is such that the map $F:\nu\to\rho_{\nu}^{\nu}$ is continuous for $\nu\in[0,\infty)$, then the set of all states ρ_{ν} defines a curve $\{\rho_{\nu}\}$ in the space of all density operators, as schematically represented in Fig. 5.1. As a result, Eq. (5.45) gives us a natural geometrical interpretation[2] for the maximal work done on a system S ($\min_{\nu}\left\{\|\rho(t)-\rho_{\nu}\|_2\right\}\|H_{\mathrm{S}}\|_2$) and the energy extracted from S ($\min_{\nu}\left\{\|\rho-\rho_{\nu}\|_2\right\}\|H_{\mathrm{S}}\|_2$): the more ρ approaches the curve $\{\rho_{\nu}\}$ at any point, the less energy can be extracted from S; on the other hand, the more $\rho(t)$ approaches $\{\rho_{\nu}\}$, the less work can be done on S.

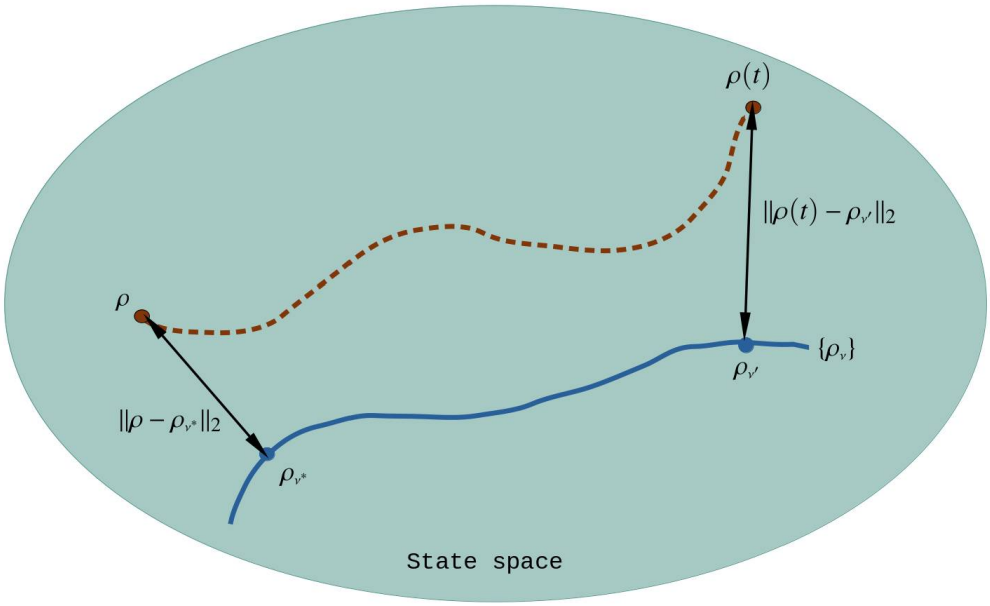


Figure 5.1 – Schematic representation in the state space (green ellipsoid) of the bounds in Eq. (5.45). The curve of all states ρ_{ν} defined in (5.17) is represented by the blue line. The universe $\mathrm{U}=\mathrm{S}+\mathrm{E}$ is prepared as ρ and is submitted to an unitary evolution ending in the state $\rho(t)$, represented by the dashed brown line. ρ_{ν^*} and $\rho_{\nu'}$ are respectively the states in the curve that approaches at most ρ and $\rho(t)$, respectively. The upper and lower bounds on work described in (5.45) are related to the distance between ρ_{ν^*} and ρ and $\rho_{\nu'}$ and $\rho(t)$, respectively.

Since the bounds (5.16), (5.28), and (5.45) are valid for sufficiently general states and dynamics, we expect them to have important applications in practical scenarios. A possible future line of research is to investigate the physical and informational interpretation of (5.45), maybe building a connection with thermodynamics practical instances.

[2] As we stated previously, we cannot determine a minimal ν for all the states, since the condition $S(\rho)=S(\rho_{\nu})$, needed to deduce the geometrical interpretation in (5.45), implies that $S(\rho)\geq\ln d_{\mathrm{E}}$. Therefore, for states in which the $S(\rho)<\ln d_{\mathrm{E}}$, the geometrical interpretation of Fig. 5.1 is not necessarily valid.

5.6 Trade-off between QM work and information

The connection between work and information theory has been investigated in many approaches analyzing how work extraction/supply can be altered when information resources are harvested [35, 71, 95, 96, 105, 143, 144]. Inspired by these works, we investigate in this section a link between QM work and the amount of available information.

Let us consider a scenario in which the average value of work is aimed to have a specified real value Ω, i.e.

$$\langle W_{\mathrm{E}\to\mathrm{S}}(t_2,t_1)\rangle = \Omega. \tag{5.46}$$

Regarding this restriction, we may ask ourselves how much information resources are needed for the average work Ω to be delivered to S. In this direction, the following result follows direct from the results of Appendix B.

Result 5.1. *The state that maximizes the von Neumann entropy, given the restriction* $\mathrm{Tr}(\rho A) = X_a$*, for a given real value* X_a *and a Hermitian operator* A*, is*

$$\rho_\nu^A := \frac{\mathrm{e}^{-\nu_a A}}{\mathcal{Z}_A^\nu}, \quad \mathcal{Z}_A^{\nu_a} = \mathrm{Tr}\left[\mathrm{e}^{-\nu_a A}\right] \tag{5.47}$$

where ν_a *is a Lagrangian multiplier, resultant from the condition* $\mathrm{Tr}\,(\rho A) = X_a$*, which must satisfy*

$$X_a = -\partial_\nu \ln \mathcal{Z}_A^\nu. \tag{5.48}$$

Moreover, the following relation is valid for any ρ *acting on* $\mathbb{H} = \mathbb{H}_\mathrm{S} \otimes \mathbb{H}_\mathrm{E}$*:*

$$\langle A\rangle - k_\mathrm{B} T_{\nu_a} S(\rho) \geq \langle A\rangle_{\nu_a} - k_\mathrm{B} T_{\nu_a} S(\rho_\nu^A). \tag{5.49}$$

where $\langle A\rangle_{\nu_a} = \mathrm{Tr}\left[\rho_\nu^A A\right]$ *and* $T_{\nu_a} = (k_\mathrm{B}\nu_a)^{-1}$*.*

From this result, we employ the substitution $A \to W_{\mathrm{E}\to\mathrm{S}}(t_2,t_1)$ and $X_a \to \Omega$ and obtain the following relation

$$\langle W_{\mathrm{E}\to\mathrm{S}}(t_2,t_1)\rangle - k_\mathrm{B} T_{\nu_w} S(\rho) \geq \langle W_{\mathrm{E}\to\mathrm{S}}(t_2,t_1)\rangle_{\nu_w} - k_\mathrm{B} T_{\nu_w} S(\rho_{\nu_w}^W), \tag{5.50}$$

with

$$\rho_{\nu_w}^W := \frac{\mathrm{e}^{-\nu_w W_{\mathrm{E}\to\mathrm{S}}(t_2,t_1)}}{\mathcal{Z}_W^{\nu_w}}, \quad \mathcal{Z}_W^{\nu_w} = \mathrm{Tr}\left[\mathrm{e}^{-\nu W_{\mathrm{E}\to\mathrm{S}}(t_2,t_1)}\right], \tag{5.51}$$

and ν_w satisfying the restriction condition

$$\Omega = -\partial_{\nu_w} \ln \mathcal{Z}_W^{\nu_w}. \tag{5.52}$$

Relation (5.50) therefore not only helps us to understand the scenarios in which (5.46) is valid but also gives us a trade-off relation between entropy and work: if we want to prepare

a state ρ, and we wish an average work Ω to be done on S during an interval $[t_1, t_2]$, then irrespective of the state ρ, its entropy must satisfy

$$S(\rho) \leq S(\rho^W_{\nu_w}). \tag{5.53}$$

In this sense, unlike the bounds deduced in the previous section, in which work is bounded given the states in the beginning and at the end of a process, here, given a prescription for work, the states are bounded so as not to surpass a maximum entropy $S(\rho^W_{\nu_w})$.

Interestingly, due to the "informational status" of the von Neumann entropy, we can consider also relation (5.50) as accounting for a trade-off between work and information. In this direction, Jaynes stated [145], when referring to the process of maximizing entropy:

"(...) in making inferences on the basis of partial information we must use that probability distribution which has maximum entropy subject to whatever is known. This is the only unbiased assignment we can make; to use any other would amount to arbitrary assumption of information which by hypothesis we do not have.".

The partial information mentioned by Jaynes is the information on the mean value, that in our case refers to the restriction (5.46), i.e., the knowledge of the mean value of work Ω. Therefore, in the direction of the Jaynes' statement, the maximization of entropy refers to the minimization of information: assuming a state other than the one that maximizes the entropy is to assume an "information which by hypothesis we do not have". Accordingly, the state $\rho^W_{\nu_w}$ is the preparation with the least amount of information that leads to a process whose work has the prescribed average value Ω during the interval $[t_1, t_2]$. In fact, this perspective can be made explicit if we consider the measure [117, 146, 147]

$$I(\rho) := \ln d - S(\rho), \tag{5.54}$$

which quantifies the information stored in the state ρ, where $d = d_{\mathrm{S}} d_{\mathrm{E}}$ denotes the dimension of the Hilbert space $\mathbb{H} = \mathbb{H}_{\mathrm{S}} \otimes \mathbb{H}_{\mathrm{E}}$. Surely, $I(\rho)$ is maximum ($\ln d$) for a pure state; in this case, "the state itself is the information" [146]. On the other hand, when ρ is completely mixed, then the information is minimum (0), characterizing a completely random state. Given the measure $I(\rho)$, relation (5.50) can be rewritten either as

$$\langle W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1)\rangle + k_{\mathrm{B}} T_{\nu_w} I(\rho) \geq \langle W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1)\rangle_{\nu_w} + k_{\mathrm{B}} T_{\nu_w} I(\rho^W_{\nu_w}), \tag{5.55}$$

or

$$\langle W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1)\rangle - \langle W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1)\rangle_{\nu_w} \geq k_{\mathrm{B}} T_{\nu_w} (I(\rho^W_{\nu_w}) - I(\rho)). \tag{5.56}$$

Taking into account Eq. (5.56) and Jaynes' statement, we may envisage the following interpretation: for an initial preparation to be able to give an exact amount of $\langle W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1)\rangle = \langle W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1)\rangle_{\nu_w} = \Omega$ of work on S, it is necessary at least an amount $I(\rho^W_{\nu_w})$ of information. If, otherwise, $I(\rho)$ is less than that, then one cannot attain a mean value Ω of work. Eq. (5.56) therefore restricts QM work done on S in terms of available information.

It is important to remark that in principle, E may be an apparatus, a bath, a Maxwell's demon or even a combination of them. Moreover, the interactions between E and S are unrestricted as well. Given the generality of the result, we want to explore in future works problems to which relation (5.56) may be relevant.

5.7 Take-away messages

In this chapter we derived some relations regarding QM work. Our results can be summarized as follows:

- By fixing the interval $[t_1, t_2]$, we can always find a Schrödinger operator corresponding to $W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1)$;
- Given the eigenbasis of energy $\{|e_i\rangle\}$ and the components $\langle e_i| H_{\mathrm{S}} |e_j\rangle$, we can describe the components $\langle e_i| W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1) |e_j\rangle$ of work, envisaging studies regarding equilibration of quantum systems;
- We derived some formal conclusions related to the special situation in which the energies at times t_1 and t_2 commutes with each other;
- We deduce the relation
$$\frac{|\langle W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1)\rangle|}{\Delta t} \leq \frac{2\sigma_H \sigma_{H_{\mathrm{S}}}^{\max}}{\hbar}$$
which bounds the time average power $\langle W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1)\rangle / \Delta t$ in terms of energy fluctuations $\sigma_H \sigma_{H_{\mathrm{S}}}^{\max}$.
- We deduce the following bounds on QM work:
$$\begin{aligned}
&\langle \mathrm{e}^{-\nu W}\rangle \geq \mathrm{e}^{-\nu(\langle W\rangle)} \geq \mathrm{e}^{-S(\rho(t)||\rho_\nu)},\\
&k_{\mathrm{B}} T_\nu S(\rho(t)||\rho_\nu) \geq \langle W\rangle \geq -k_{\mathrm{B}} T_\nu S(\rho||\rho_\nu)\\
&\min_\nu \{\|\rho(t) - \rho_\nu\|_2\} \|H_{\mathrm{S}}\|_2 \geq \langle W\rangle \geq -\min_\nu \{\|\rho - \rho_\nu\|_2\} \|H_{\mathrm{S}}\|_2,
\end{aligned}$$
with the last relation enabling us to envisage a geometrical interpretation in the state space for fairly general (not necessarily thermodynamics) scenarios;
- We deduced the relation
$$\langle W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1)\rangle - \langle W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1)\rangle_{\nu_w} \geq k_{\mathrm{B}} T_{\nu_w} (I(\rho_{\nu_w}^W) - I(\rho)),$$
which makes explicit a trade-off between work and information, where a minimum amount of stored information is needed for an specific amount of work to be done on a system.

Throughout this chapter, we envisaged several possible lines of future research regarding, as starting points, the relations deduced here. We hope that these preliminary findings may serve as inspiration for other possible approaches.

6 Fluctuation theorems for a mechanical work observable

As discussed in Sections 2.2 and 2.3, fluctuation theorems (FTs) have been extended from the filed of stochastic thermodynamics to general quantum scenarios. Within the regarded fluctuating quantities, work plays a prominent role because of its key relevance for complete statements of the energy conservation law. Paramount for an unambiguous definition of work is the specification of both the *agent* (the acting system), the one that applies the driving force, and the *receiver* (the system acted upon), the one which the force is applied on. However, as we reviewed in Chapter 2, the research about the consequences for work FTs of taking the agent as a genuine quantum system has remained elusive. Indeed, despite the developments, the literature still lacks a proper picture for the agent's role to FTs; the relevance of nontrivial states, eventually encoding correlations with the receiver or subjected to thermal effects, has remained unexplored. For instance, taking W as the work done by the agent on the receiver, how does $\langle \mathrm{e}^{-\beta_1 W} \rangle$ compare with either Jarzinsky (Eq. (2.20))

$$\langle \exp(-\beta \mathcal{W}_{\mathrm{hb}}(t,0)) \rangle = \mathcal{Z}_t / \mathcal{Z}_0, \tag{6.1}$$

or BK (Eq. (2.23))

$$\langle \exp(-\beta \mathcal{W}_{\mathrm{E}\to\mathrm{S}}) \rangle = 1 \tag{6.2}$$

equalities for an arbitrary agent's state?

Our main goal in the present chapter is to analyze the situation under *mechanical* lenses. Specifically, we assess the dependence of the quantity $\langle \mathrm{e}^{-\beta_1 W} \rangle$ on the agent's reduced state, in both classical and quantum contexts, for the specific system of two particles interacting through an elastic potential within a particular time interval $[t_1, t_2]$. The result is compared with the BK equality (6.2), which is closer than Jarzynski's (6.1) in the mechanical context. The classical scenario is studied using the usual Newtonian notion of work with its statistics being computed in accordance with Liouvillian framework. For the analysis in the corresponding quantum scenario, we employ the QM work introduced in Chapter 3. We demonstrate by explicit examples that quantum phenomena, such as entanglement and coherence, indeed affect the BK equality. The adequacy of the comparison is ensured by taking the receiver's initial state as thermal, with inverse temperature β. Equally interesting is the role found for the agent's *inertia*, which emerges, already in the classical context, from the fact that our approach is genuinely autonomous and, hence, do not rely on the figure of an "infinite mass" driving system.

6.1 Classical autonomous scenario

Consider two particles of masses $m_{1,2}$ interacting via an elastic potential of characteristic constant k. The classical autonomous dynamics is governed by the Hamiltonian function

$$\mathcal{H} = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + \frac{k}{2}(x_2 - x_1)^2, \tag{6.3}$$

where x_i (p_i) is the position (momentum) of the i-th particle. Henceforth, particle 1 (2) will be called the *receiver* (*agent*). In accordance with Section 2.1, within the mechanical perspective, the work $\mathcal{W}(t_2, t_1)$ done by particle 2 on particle 1, henceforth referred to as agent's work, during the time interval $[t_1, t_2]$, is defined as

$$\mathcal{W}(t_2, t_1) := \int_{t_1}^{t_2} \mathrm{d}t \; m_1 \ddot{x}_1 \, \dot{x}_1 = \Delta\mathcal{K}, \tag{6.4}$$

where $\Delta\mathcal{K} = \mathcal{K}_1(t_2) - \mathcal{K}_1(t_1)$ with $\mathcal{K}_1(t) = \frac{m_1 \dot{x}_1^2(t)}{2}$ being the kinetic energy of particle 1 (receiver's internal energy). Aiming at computing statistics of $\mathcal{W}(t_2, t_1)$, we solve the Hamilton equations to obtain explicit expressions in terms of the initial phase point $\Gamma_0 = (x_1^0, p_1^0, x_2^0, p_2^0) \equiv (x_1(0), p_1(0), x_2(0), p_2(0))$. In analogy with Eq. (3.14) in the quantum scenario depicted in Section 3.2.2, we introduce the usual relative-center of mass (classical) transformation

$$\begin{aligned} x_{\mathrm{cm}} &= (m_1 x_1 + m_2 x_2)/M, \\ x_{\mathrm{r}} &= x_2 - x_1, \\ p_{\mathrm{cm}} &= p_1 + p_2, \\ p_{\mathrm{r}} &= \mu \left(p_2/m_2 - p_1/m_1 \right), \end{aligned} \tag{6.5}$$

where, again, $\mu = m_1 m_2 / M$ and $M = m_1 + m_2$, so that we can rewrite the Hamiltonian function as $\mathcal{H} = p_{\mathrm{cm}}^2/2M + p_{\mathrm{r}}^2/2\mu + k x_{\mathrm{r}}^2/2$, decoupling the center-of-mass variables dynamics from the relative one. As a consequence, one can describe the time-evolution of the center of mass and of relative coordinates individually, which then yields the solutions

$$\begin{aligned} x_{\mathrm{cm}}^t &= x_{\mathrm{cm}}^0 + p_{\mathrm{cm}}^0 t/M, \\ x_{\mathrm{r}}^t &= x_{\mathrm{r}}^0 \cos(\omega t) + (p_{\mathrm{r}}^0/\mu\omega) \sin(\omega t), \\ p_{\mathrm{cm}}^t &= p_{\mathrm{cm}}^0, \\ p_{\mathrm{r}}^t &= p_{\mathrm{r}}^0 \cos(\omega t) - \mu\omega x_{\mathrm{r}}^0 \sin(\omega t), \end{aligned} \tag{6.6}$$

with $\omega = \sqrt{k/\mu}$. Returning to the original variables, we can write a expression for the momentum of particle 1 at a time t,

$$p_1^t(\Gamma_0) = a(t)\, p_1^0 + b(t)\, p_2^0 + c(t) \left(x_2^0 - x_1^0 \right), \tag{6.7}$$

$$\begin{cases} a(t) = \left[m_1 + m_2 \cos(\omega t) \right] / M, \\ b(t) = \left[1 - \cos(\omega t) \right] m_1 / M, \\ c(t) = \mu\omega \sin(\omega t). \end{cases} \tag{6.8}$$

As a result, we are able to write explicit expressions for the kinetic energy $\mathcal{K}_1(t)$ and the work $\mathcal{W}(t_2,t_1)$ as functions of the initial phase point Γ_0. For simplicity, hereafter we restrict our analysis to time intervals such as $[t_1,t_2]=[0,v\tau]$, with $\tau=\pi/\omega$ and v an odd integer, and introduce the shorter notation $\mathcal{W}(\Gamma_0)\equiv\mathcal{W}(v\tau,0)$. This gives

$$\mathcal{W}(\Gamma_0)=\frac{2}{M^2}(m_1p_2^0-m_2p_1^0)(p_1^0+p_2^0). \tag{6.9}$$

To raise the work statistics, we consider an initial distribution $\varrho(\Gamma_0)$, so that the mean value of any sufficiently smooth function $f(\mathcal{W}(\Gamma_0))$ of work can be computed as

$$\langle f(\mathcal{W})\rangle_\varrho=\int_{\Gamma_0}\mathrm{d}\Gamma_0\, f(\mathcal{W}(\Gamma_0))\,\varrho(\Gamma_0). \tag{6.10}$$

Focusing on scenarios associated with the BK equality, we start by considering, as our first case study, the initial thermal-Gaussian (TG) distribution

$$\varrho_{\mathrm{TG}}(\Gamma_0)=\mathcal{T}_{\Delta_1}(x_1^0,p_1^0)\;\mathcal{G}_{\bar{\mathbf{r}}_2,\sigma_2}(x_2^0,p_2^0), \tag{6.11}$$

which assigns to the receiver the thermal distribution

$$\mathcal{T}_\Delta(x,p):=\frac{\exp\left(-\frac{p^2}{2\Delta^2}\right)}{\sqrt{2\pi\Delta^2}}\,\varrho(x), \tag{6.12}$$

where $\Delta:=\sqrt{m/\beta}$ is the "thermal momentum uncertainty", β is the inverse temperature, and $\varrho(x)$ is a generic probability distribution[1]. By its turn, the agent is given the Gaussian distribution $\mathcal{G}_{\bar{\mathbf{r}},\sigma}(x,p)\equiv\mathcal{G}_{\bar{x},\sigma_x}(x)\,\mathcal{G}_{\bar{p},\sigma}(p)$, with $\bar{\mathbf{r}}=(\bar{x},\bar{p})$, $\sigma_x=\frac{\hbar}{2\sigma}$, and

$$\mathcal{G}_{\bar{u},\sigma_u}(u)=\frac{\exp\left[-\frac{(u-\bar{u})^2}{2\sigma_u^2}\right]}{\sqrt{2\pi\sigma_u^2}}, \tag{6.13}$$

where $\bar{u}$ and σ_u denote the centroid and the width of the Gaussian distribution, respectively. Given the distribution (6.11), the averaging prescribed by (6.10) for the function $f(\mathcal{W}(\Gamma_0))=\mathrm{e}^{-\beta\mathcal{W}(\Gamma_0)}$ results in

$$\langle\mathrm{e}^{-\beta_1\mathcal{W}}\rangle_{\varrho_{\mathrm{TG}}}=\frac{m_1+m_2}{|m_1-m_2|}. \tag{6.14}$$

In comparison with the BK formula (6.2), the differences are clear and insightful, specially with regard to the finite inertia of the agent. Notably, the BK formula is recovered as $\frac{m_1}{m_2}\to 0$, limit in which $x_2^t\to x_{\mathrm{cm}}^t=x_{\mathrm{cm}}^0+p_{\mathrm{cm}}^0t/m_2$. This is the exact regime for which the BK equality was deduced, *viz.* the one that presuming that the agent acts as a deterministic classical driven whose dynamics can in no way be disturbed by the receiver. Therefore, the dependence of the result (6.14) on the masses is a direct consequence of the autonomous character of the dynamics under scrutiny. Also noticeable is the fact that (6.14) does not

[1] We could, for instance, choose $\varrho(x)$ so to characterize a particle confined in a box, as usually done in thermodynamics context [39, 148].

depend on the details of the preparation, such as $\bar{\mathbf{r}}_2$, σ_2, and $\Delta_1 = \sqrt{m_1/\beta_1}$. This may be a consequence of the quadratic structure of the model and eventual peculiarities underlying the time interval chosen. In any case, this reveals that, as long as the condition $m_2 \gg m_1$ is satisfied, the BK equality holds even in the regime of highly fluctuating agent distributions, for which the notion of a deterministic classical control can no longer be ensured.

We now conduct our second case study, in which both the receiver and agent are initially given thermal states with respective inverse temperatures β_1 and β_2. The composite thermal-thermal (TT) distribution then reads

$$\varrho_{\mathrm{TT}}(\Gamma_0) = \mathcal{T}_{\Delta_1}(x_1^0, p_1^0)\ \mathcal{T}_{\Delta_2}(x_2^0, p_2^0), \tag{6.15}$$

where $\Delta_i = \sqrt{m_i/\beta_i}$ with $i \in \{1,2\}$. Through similar calculations, we find the same result, that is, $\langle \mathrm{e}^{-\beta_1 \mathcal{W}} \rangle_{\varrho_{\mathrm{TG}}} = \langle \mathrm{e}^{-\beta_1 \mathcal{W}} \rangle_{\varrho_{\mathrm{TT}}}$. Clearly, once again the inertial aspects prevails over any other elements of the preparation, even the arbitrary temperatures $\beta_{1,2}$.

The situation gets more interesting when we get to our third case study. Here we let not only thermal ingredients be present but also correlations. The initial distribution is chosen to be

$$\varrho_c(\Gamma_0) = \mathcal{T}_{\Delta_1}(x_1^0, p_1^0)\ \varrho_x(x_2^0)\delta_{\mathrm{D}}(p_2^0 - c p_1^0), \tag{6.16}$$

where δ_{D} denotes the Dirac delta function, c is a dimensionless parameter whose role is discussed below, and again $\varrho_x(x_2^0)$ is a generic probability distribution. It is not difficult to check that the marginals are thermal distributions:

$$\varrho_i(x_i^0, p_i^0) \equiv \iint \mathrm{d}x_j^0 \mathrm{d}p_j^0\, \varrho_c(\Gamma_0) = \mathcal{T}_{\Delta_i}(x_i^0, p_i^0), \tag{6.17}$$

with $i,j \in \{1,2\}$ and $j \neq i$. An interesting aspect is the appearance of the local inverse temperature $\beta_2(c) \equiv \frac{\beta_1}{c^2}\frac{m_2}{m_1}$ deriving from the connection $\Delta_2 = |c|\Delta_1$. We see, therefore, that $|c|$ is a direct estimate of both the correlations between the particles and the agent's thermal momentum uncertainty. Through the same procedure adopted previously, we arrive at

$$\langle \mathrm{e}^{-\beta_1 \mathcal{W}} \rangle_{\varrho_c} = \frac{m_1 + m_2}{|m_1 - m_2 + 2m_1 c|}. \tag{6.18}$$

In direct comparison with (6.14), the above result demonstrates that classical correlations can influence work FTs in a relevant way. In particular, for $m_1 = m_2$, one has $\langle \mathrm{e}^{-\beta_1 \mathcal{W}} \rangle_{\varrho_c} = \frac{1}{|c|} = \sqrt{\beta_2/\beta_1}$, which makes explicit the strong dependence of the result also on the local temperatures. From a broader perspective, result (6.18) reveals an interesting generalization of the BK formula: by getting apart from the typical thermodynamics setting wherein the agent is a deterministic driver, we find that work FTs can strongly depend on both inertia and, via correlations, agent's effective temperature, $T_2 = [k_B \beta_2(c)]^{-1}$.

6.2 Quantum autonomous scenario

In full analogy with the classical model studied in the previous section, we consider again particles of masses $m_{1,2}$ evolving autonomously under the unitary dynamics implied by the Hamiltonian operator

$$H = \frac{P_1^2}{2m_1} + \frac{P_2^2}{2m_2} + \frac{k}{2}(X_2 - X_1)^2, \tag{6.19}$$

where X_i (P_i) is the position (momentum) operator of the i-th particle. The quantum preparation ρ and H act on the joint Hilbert space $\mathbb{H} = \mathbb{H}_1 \otimes \mathbb{H}_2$, as before.

As we are interested in exploring FTs under a mechanical perspective, we employ the QM work definition of Chapter 3. As before, particle 1 (2) will play the role of the receiver (agent). The QM work operator delivered by the agent to the receiver within a time interval $[t_1, t_2]$ is then defined as

$$W_{2\to 1}(t_2, t_1) \coloneqq \int_{t_1}^{t_2} \mathrm{d}t \; m_1 \frac{\{\dot{X}_1, \ddot{X}_1\}}{2} = \Delta K, \tag{6.20}$$

where $\Delta K = K_1(t_2) - K_1(t_1)$, with $K_1(t) = \frac{m_1 \dot{X}_1^2}{2}$ being the kinetic energy of particle 1 (receiver's internal energy). Here, as in Section 3.2.2, we can also decouple the Hamiltonian operator as $H = P_{\mathrm{cm}}^2/2M + P_{\mathrm{r}}^2/2\mu + kX_{\mathrm{r}}^2/2$, by means of the operator transformation

$$\begin{aligned} X_{\mathrm{cm}} &= (m_1 X_1 + m_2 X_2)/M, \\ X_{\mathrm{r}} &= X_2 - X_1, \\ P_{\mathrm{cm}} &= P_1 + P_2, \\ P_{\mathrm{r}} &= \mu\,(P_2/m_2 - P_1/m_1)\,. \end{aligned} \tag{6.21}$$

As in the classical model, the analytical solutions allow us to write

$$P_1(t) = a(t)\, P_1^{\mathrm{s}} + b(t)\, P_2^{\mathrm{s}} + c(t)\,(X_2^{\mathrm{s}} - X_1^{\mathrm{s}})\,, \tag{6.22}$$

with the same functions $a(t)$, $b(t)$ and $c(t)$ defined in (6.8). Restricting again our analysis to the time interval $[t_1, t_2] = [0, v\tau]$, with $\tau = \pi/\omega$ and v an odd integer, and introducing the shorter notation $W = W_{2\to 1}(v\tau, 0)$, we find

$$W = \frac{2}{M^2}(m_1 P_2^{\mathrm{s}} - m_2 P_1^{\mathrm{s}})(P_1^{\mathrm{s}} + P_2^{\mathrm{s}}) \tag{6.23}$$

for the operator work done by the agent on the receiver during $[0, v\tau]$, where, similarly to Eq. (3.19) of Chapter 3, its eigenvalues can be expressed as

$$w_{p_1,p_2} = \frac{2}{M^2}(m_1 p_2 - m_2 p_1)(p_1 + p_2) \tag{6.24}$$

in terms of the joint momentum basis $\{|p_1, p_2\rangle\}$. Having computed the work observable (6.23), we can raise the statistics associated with any sufficiently smooth function $f(W)$ for an initial state ρ acting on the joint space $\mathbb{H}$ via

$$\langle f(W)\rangle_\rho = \iint \mathrm{d}p_1 \mathrm{d}p_2\, f(w_{p_1,p_2})\, \varrho(p_1, p_2), \tag{6.25}$$

where $\varrho(p_1,p_2)=\langle p_1,p_2|\rho|p_1,p_2\rangle$. In what follows, we analyze the expectation value of the operator $f(W)=\mathrm{e}^{-\beta_1 W}$ in instances analogous to those considered in the classical context, but also in exclusively quantum scenarios. Details of the calculations are presented in the Appendix C.

Let us start with the case involving a thermal-Gaussian state given by

$$\rho_{\mathrm{TG}}=T_{\Delta_1}(\sigma_1)\otimes G_{\bar{\mathbf{r}}_2,\sigma_2}, \tag{6.26}$$

where $G_{\bar{\mathbf{r}}_2,\sigma_2}=|\bar{\mathbf{r}}_2\rangle\langle\bar{\mathbf{r}}_2|$ denotes a pure Gaussian state, meaning that

$$\begin{aligned}\langle x_2|\bar{\mathbf{r}}_2\rangle&=\left(\frac{2\sigma_2^2}{\pi\hbar^2}\right)^{1/4}\mathrm{e}^{-\frac{\sigma_2^2(x_2-\bar{x}_2)^2}{\hbar^2}+\frac{i\bar{p}_2x_2}{\hbar}},\\ \langle p_2|\bar{\mathbf{r}}_2\rangle&=\frac{1}{\left(2\pi\sigma_2^2\right)^{1/4}}\mathrm{e}^{-\frac{(p_2-\bar{p}_2)^2}{4\sigma_2^2}-\frac{i(p_2-\bar{p}_2)\bar{x}_2}{\hbar}},\end{aligned} \tag{6.27}$$

where $\bar{\mathbf{r}}_2=(\bar{x}_2,\bar{p}_2)$. For the receiver, we consider the effective thermal state

$$T_{\Delta_1}(\sigma_1)=\int\mathrm{d}p\,\frac{\mathrm{e}^{-\frac{p^2}{2\Delta_1^2}}}{\sqrt{2\pi\Delta_1^2}}\,G_{(0,p),\sigma_1}, \tag{6.28}$$

where we recall that $\Delta_1=\sqrt{m_1/\beta_1}$. Able to avoid the singularities and normalization problems typical of continuum bases and being very convenient for the sake of analytical computations, this state actually is just an approximation to a genuine thermal state with inverse temperature β_1. In effect, as we show in the Appendix C, whenever $\frac{\sigma_1}{\Delta_1}\ll 1$ one has

$$\begin{aligned}\langle p_1|T_{\Delta_1}(\sigma_1)|p_1\rangle&\cong\sqrt{\frac{\beta_1}{2\pi m_1}}\,\mathrm{e}^{-\frac{\beta_1 p_1^2}{2m_1}},\\ \langle p_1'|T_{\Delta_1}(\sigma_1)|p_1\rangle&\cong 0\qquad\text{if }\ p_1'\neq p_1.\end{aligned} \tag{6.29}$$

That is, when the momentum fluctuation σ_1 of the Gaussian states $G_{(0,p),\sigma_1}$ is much smaller than the thermal fluctuation Δ_1, then $T_{\Delta_1}(\sigma_1)$ approaches a fully incoherent mixture (in the kinetic energy basis) with thermal populations given by (6.29). Consequently, in the the regime where $\frac{\sigma_1}{\Delta_1}\to 0$, ρ_{TG} as defined by (6.26) is a reasonable quantum analogue of ϱ_{TG} as given by (6.11). Following the prescription indicated by (6.25), with $f(W)=\mathrm{e}^{-\beta_1 W}$, $\sigma_1\ll\Delta_1$, and finite σ_1, we find

$$\left\langle\mathrm{e}^{-\beta_1 W}\right\rangle_{\rho_{\mathrm{TG}}}\cong\frac{m_1+m_2}{|m_1-m_2|}, \tag{6.30}$$

which is identical to the classical result (6.14). (See the Appendix C for details of the calculations and appreciation of the complete result which reduces to the above one.) Again, inertia plays a role in the fluctuation relation and BK's formula for the nonautonomous scenario is readily retrieved for $m_2\gg m_1$. It is worth noticing, however, the BK context is

strictly implemented only when, in addition to $m_2 \gg m_1$, we consider a dispersion-free state for the agent.

An interesting situation occurs when not only $\sigma_1 \ll \Delta_1$ but also $\Delta_1 \ll \sigma_2$. In this case, while the receiver's state becomes nearly thermal, the agent gets spatial localization. In this regime, we have (see the Appendix C)

$$\langle \mathrm{e}^{-\beta_1 W} \rangle_{\rho_{\mathrm{TG}}} \cong \frac{m_1 + m_2}{|m_1 - m_2|} \Gamma, \tag{6.31}$$

where $\Gamma \equiv \left[1 - \left(\frac{2m_1\gamma}{m_1 - m_2}\right)^2\right]^{-\frac{1}{2}}$ and $\gamma \equiv \sigma_1\sigma_2/\Delta_1^2$ (as shown in the Appendix C, γ is bounded so as to guarantee that Γ is real). We see that, in this regime, the agent's quantum uncertainties significantly influence the work fluctuation relation.

In analogy with the classical distribution (6.15), our next case study focus on the effective thermal-thermal state

$$\rho_{\mathrm{TT}} = T_{\Delta_1}(\sigma_1) \otimes T_{\Delta_2}(\sigma_2), \tag{6.32}$$

where $T_{\Delta_i}(\sigma_i)$ have precisely the same structure as (C.3). When $\sigma_i \ll \Delta_i$ these reduced states become thermal, with respective inverse temperatures β_i, in the sense delineated by (6.29). As in the classical instance, here we can show that $\langle \mathrm{e}^{-\beta_1 W} \rangle_{\rho_{\mathrm{TG}}} = \langle \mathrm{e}^{-\beta_1 W} \rangle_{\rho_{\mathrm{TT}}}$.

We now consider the correlated state

$$\rho_c = \int \mathrm{d}p \, \frac{\mathrm{e}^{-\frac{p^2}{2\Delta_1^2}}}{\sqrt{2\pi\Delta_1^2}} G_{(0,p),\sigma} \otimes G_{(0,cp),\sigma} \tag{6.33}$$

where $c > 0$ correlates the momenta of the particles, in analogy with the scenario defined by (6.16). As shown in the Appendix C, whenever the momentum fluctuation of both Gaussian states is small enough ($\sigma \ll \Delta_1$), then the reduced states $\rho_1 = \mathrm{Tr}_2\, \rho_c$ and $\rho_2 = \mathrm{Tr}_1\, \rho_c$ can be locally identified as thermal, with inverse temperatures β_1 and $\beta_2 = \frac{\beta_1}{c^2}\frac{m_2}{m_1}$, respectively. In this regime, we find

$$\langle \mathrm{e}^{-\beta_1 W} \rangle_{\rho_c} \cong \frac{m_1 + m_2}{|m_1 - m_2 + 2m_1 c|}, \tag{6.34}$$

which agrees with the classical expression (6.18). Maybe not so surprisingly, we have thus far found a complete match between classical and quantum predictions with regard to work FTs within a mechanical perspective. Next, we analyze scenarios with no classical counterpart.

6.2.1 Agent in quantum superposition

Let us consider the preparation

$$\rho_{\mathrm{TS}} = T_{\Delta_1}(\sigma_1) \otimes \frac{(\xi + \chi)}{N}, \tag{6.35}$$

where

$$\begin{aligned} \xi &= |\bar{\mathbf{r}}_2\rangle \langle \bar{\mathbf{r}}_2| + |\bar{\mathbf{r}}_2'\rangle \langle \bar{\mathbf{r}}_2'|, \\ \chi &= |\bar{\mathbf{r}}_2\rangle \langle \bar{\mathbf{r}}_2'| + |\bar{\mathbf{r}}_2'\rangle \langle \bar{\mathbf{r}}_2|, \end{aligned} \tag{6.36}$$

with $|\bar{\mathbf{r}}_2\rangle$ and $|\bar{\mathbf{r}}_2'\rangle$ Gaussians state with center at $\bar{\mathbf{r}}_2 = (\bar{x}_2, \bar{p}_2)$ and $\bar{\mathbf{r}}_2' = \bar{\mathbf{r}}_2 + (\delta_x, 0)$, respectively, and momentum uncertainty σ_2. δ_x is a generic spatial displacement and the normalization factor is given $N = \mathrm{Tr}\,(\chi + \xi) = 2\big[1 + \exp(-\frac{\delta_x^2\sigma_2^2}{2\hbar^2})\big]$.

Implementing a superposition of Gaussian states for the agent, state (6.36) allows us to investigate whether coherence can play some role to the work FT. As proved in the Appendix C, this is not the case when $\sigma_1 \ll \Delta_1$, for in this case we obtain

$$\langle \mathrm{e}^{-\beta_1 W}\rangle_{\rho_{\mathrm{TS}}} \cong \frac{m_1 + m_2}{|m_1 - m_2|}, \tag{6.37}$$

This is the same expression as (6.30), which means that, with regard to the fluctuation relation, in this regime (and time interval) it is completely immaterial whether we consider the thermal-Gaussian state ρ_{TG} or the thermal-superposition state ρ_{TS}.

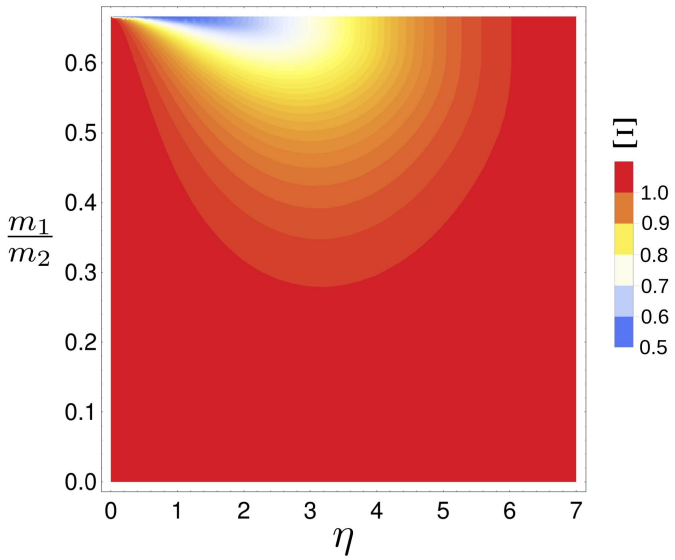


Figure 6.1 – Attenuation factor Ξ as a function of the mass ratio m_1/m_2 and $\eta = 2\sigma_2\delta_x/\hbar$ (which predicts an observable interference pattern as η becomes small), in the regime $\sigma_1 \ll \Delta_1 \ll \sigma_2$, for $\gamma = 0.25$. The combined effects of inertia and interference are seen to be mostly significant in the upper half of the panel.

On the other hand, if we consider in addition that $\sigma_2 \gg \Delta_1$, so that $|\bar{\mathbf{r}}_2\rangle$ and $|\bar{\mathbf{r}}_2'\rangle$ turn out to be extremely sharp Gaussian states, then we get

$$\langle \mathrm{e}^{-\beta_1 W}\rangle_{\rho_{\mathrm{TS}}} \cong \frac{(m_1 + m_2)}{|m_1 - m_2|}\,\Gamma\,\Xi, \tag{6.38}$$

where $\Xi \equiv \frac{1+\exp\left(-\eta^2\Gamma^2/8\right)}{1+\exp(-\eta^2/8)}$ and $\eta \equiv 2\sigma_2\delta_x/\hbar$. Note that η dictates whether a spatial interference pattern is detectable for the preparation: if $\eta \gg 1$, meaning that the distance δ_x between the wave packets is much greater than their width $\frac{\hbar}{2\sigma_2}$, then no interference pattern is visible, although the agent's initial state is a coherent superposition. In this case, one has $\Xi \simeq 1$, and the expression (6.38) reduces to (6.31), which can be shown to be the fluctuation relation also when the agent state is the mixture $\xi/2$. On the other hand, if η is not too big, so that interference is observable for the agent's initial state, then Ξ becomes

smaller than unit and the fluctuation relation is significantly influenced by agent's spatial coherence[2]. It can readily be seen from the plot of Ξ as a function of η and m_1/m_2 in Figure 6.1 how interference and inertia effects can be combined to maximally influence the work fluctuation relation. Interference becomes most important when, to begin with, it meets the conditions to exist in the preparation (η small) and when the ratio of masses comes closer to its upper bound $(1+2\gamma)^{-1}$, regime which maximally departs from the scenario of a classical heavy agent. Finally, as discussed in the Appendix C, the role of interference is shown to be significant also in a regime where the agent's average momentum is large, that is, $\bar{p}_2 \gg \Delta_1$.

6.2.2 Agent entangled with receiver

Finally, we consider an entangled initial state $\rho_{\mathfrak{e}} = |\psi\rangle\langle\psi|$, where

$$|\psi\rangle = \int \mathrm{d}p \, \frac{\mathrm{e}^{-\frac{p^2}{4\Delta_1^2}}}{\sqrt{N}} \, |0,p\rangle \otimes |\mathfrak{e}p,0\rangle \,, \tag{6.39}$$

$\Delta_1 = \sqrt{m_1/\beta_1}$ again, N is a normalization constant, $|0,p\rangle$ is a receiver's Gaussian state with center at the mean phase space point $\bar{\mathbf{r}}_1 = (0,p)$ and momentum uncertainty σ_1, $|\mathfrak{e}p,0\rangle$ is an agent's Gaussian state with center at the mean phase space point $\bar{\mathbf{r}}_2 = (\mathfrak{e}p,0)$ and momentum uncertainty σ_2. Whenever nonzero, the parameter $\mathfrak{e}$ regulates the correlation of the receiver's momentum with the agent's position. In the limits $\sigma_1 \to 0$ and $\sigma_2 \to \infty$, the Gaussian states $|0,p\rangle$ and $|\mathfrak{e}p,0\rangle$ approach momentum and position eigenstates, for the respective particles, with $|\psi\rangle$ thus representing a highly entangled state.

As shown in the Appendix C, for $\sigma_1 \ll \Delta_1$ the reduced states $\rho_{1,2}$ satisfy the relations

$$\begin{aligned} \langle p_1|\rho_1|p_1\rangle &\cong \sqrt{\frac{\beta_1}{2\pi m_1}} \, \mathrm{e}^{-\frac{\beta_1 p_1^2}{2m_1}}, \\ \langle p_1'|\rho_1|p_1\rangle &\cong 0 \quad \text{if } \; p_1' \neq p_1, \end{aligned} \tag{6.40}$$

and

$$\begin{aligned} \langle x_2|\rho_2|x_2\rangle &\cong \frac{1}{\sqrt{2\pi\Delta_{\mathfrak{e}}^2}} \, \mathrm{e}^{-\frac{x_2^2}{2\Delta_{\mathfrak{e}}^2}}, \\ \langle x_2'|\rho_2|x_2\rangle &\cong 0 \quad \text{if } \; x_2' \neq x_2. \end{aligned} \tag{6.41}$$

where $\Delta_{\mathfrak{e}} \equiv \mathfrak{e}\Delta_1$. Therefore, not only ρ_1 is effectively thermal but also ρ_2 approximates a mixture of position eigenstates with Gaussian weights of mean value 0 and dispersion $\Delta_{\mathfrak{e}}$. It is also shown in the Appendix C that, up to the first order of $\frac{\sigma_1}{\Delta_1}$, the amount E of

[2] It is worth remarking that the implications of agent's spatial coherence to the work fluctuation relation cannot be thought of as emerging from local elements solely. To see this note that if $\gamma = \sigma_1\sigma_2/\Delta_1^2$ (a "nonlocal" parameter) could assume vanishing values, then $\Gamma \simeq 1$ and $\Xi \simeq 1$, so that no influence of coherence survives.

entanglement encoded in the initial state ρ_{E} results, in terms of the linear entropy $1-\mathrm{Tr}\,\rho_i^2$ ($i\in\{1,2\}$), in

$$E(\rho_{\mathfrak{e}})\cong 1-\frac{\sigma_1}{\Delta_1}\sqrt{1+\vartheta_{\mathfrak{e}}^2}, \tag{6.42}$$

where $\vartheta_{\mathfrak{e}}\equiv\hbar/(2\mathfrak{e}\sigma_1\sigma_2)$. (The exact formula derived in the Appendix C indeed predicts that $E=0$ for $\mathfrak{e}=0$, as expected, but the approximation above does not hold for vanishing values of $\mathfrak{e}$.) As mentioned previously, the entanglement becomes maximum as $\frac{\sigma_1}{\Delta_1}\to 0$. Close to this limit, it holds that

$$\langle \mathrm{e}^{-\beta_1 W}\rangle_{\rho_{\mathfrak{e}}}\cong\frac{m_1+m_2}{\sqrt{(m_1-m_2)^2-\frac{\hbar^2\beta_1^2}{\mathfrak{e}^2(1+\vartheta_{\mathfrak{e}}^2)}}}, \tag{6.43}$$

which shows that entanglement disturbs the work fluctuation relation. It is interesting to assess whether purely classical correlations would also cause a similar perturbation. To this end, we consider the classically correlated state

$$\rho_{\mathfrak{c}}=\int\mathrm{d}p\,\frac{\mathrm{e}^{-\frac{p^2}{2\Delta_1^2}}}{\sqrt{2\pi\Delta_1^2}}G_{(0,p),\sigma_1}\otimes G_{(\mathfrak{c}p,0),\sigma_2}, \tag{6.44}$$

which has the same form as ρ_c in (6.33), but here the momentum of particle 1 is classically correlated with the position (instead of the momentum) of particle 2 through the parameter $\mathfrak{c}$. Considering once again the regime in which $\sigma_1\ll\Delta_1$, we arrive at

$$\langle \mathrm{e}^{-\beta_1 W}\rangle_{\rho_{\mathfrak{c}}}\cong\frac{m_1+m_2}{\sqrt{(m_1-m_2)^2-\frac{\hbar^2\beta_1^2}{\mathfrak{c}^2\vartheta_{\mathfrak{c}}^2}}}, \tag{6.45}$$

where $\vartheta_{\mathfrak{c}}=\hbar/(2\mathfrak{c}\sigma_1\sigma_2)$. The formal comparison with result (6.43) is immediate. In particular, we see that the scenarios are comparable when $\vartheta_{\mathfrak{e},\mathfrak{c}}\gg 1$, while respecting the nonnegativity of entanglement in (6.42). Also noteworthy is the fact that $\hbar^2\beta_1^2/(\mathfrak{c}^2\vartheta_{\mathfrak{c}}^2)=(2\beta_1\sigma_1\sigma_2)^2$, which shows that (6.45) is $\hbar$-independent and, therefore, can be claimed to be a fundamentally classical result. In any case, though, it is clear that quantum and purely classical correlations, in combination with thermal and inertial aspects, generally have different impacts in the work FT. This difference disappears as $\hbar\beta_1/m_2$ is sufficiently small, for in this regime both (6.43) and (6.45) coalesce to the typical form $(m_1+m_2)/|m_1-m_2|$. Moreover, BK's formula is retrieved as $m_1\ll m_2$.

Before closing this section, two remarks are in order. First, work FTs are commonly associated with contexts involving two-point measurement (TPM) protocols and incoherent states in the energy basis [21,31,65], so it is opportune to ask how such protocols compare with the current approach. In the Appendix C we show that application of a given TPM protocol, suitably adapted to our mechanical autonomous scenario, lead to a result that can only be consistent with $\langle \mathrm{e}^{-\beta_1 W}\rangle_{\rho_{\mathfrak{c}}}$, for both initial states $\rho_{\mathfrak{e},\mathfrak{c}}$, being thus unable to reproduce the predictions given by $\langle \mathrm{e}^{-\beta_1 W}\rangle_{\rho_{\mathfrak{e}}}$. Second, direct application of Jensen's inequality,

$\langle e^{-\beta_1 W}\rangle_\rho \geqslant e^{-\beta_1 \langle W\rangle_\rho}$, allows us to write

$$\langle W\rangle_\rho \geqslant \Delta\mathscr{F} \equiv -\frac{1}{\beta_1}\ln\langle e^{-\beta_1 W}\rangle_\rho\,, \tag{6.46}$$

where $\Delta\mathscr{F}$ is a lower bound for the average mechanical work done by the agent on the receiver. While the BK equality (6.2) imposes that the average work can never be negative in any time interval, here we have shown that there exist time intervals wherein $\Delta\mathscr{F}$ can assume negative values. This means that, within the present perspective in which work is a Hermitian operator and the system is autonomous, then a finite-mass agent can also draw energy from the receiver.

6.3 Take-away messages

Crucial to the assessment of physical systems' responses to applied external perturbations, FTs allow us to analyze averages of fluctuating quantities in terms of physical aspects imposed by equilibrium. These studies, however, are typically conducted under classical-like assumptions, and searching for eventual effects of relaxing such constraints is vital for one to build a better comprehension of non-equilibrium thermodynamics.

In this chapter, we avoided classicalities in several ways; we considered (i) an exclusive work observable, (ii) a finite-mass agent, (iii) an autonomous agent-receiver dynamics, and (iv) fundamentally quantum global states which are thermal only locally. Then, we computed work FTs for a specific time interval and compared our results with the BK formula (6.2). Interestingly, we have been able to show that quantum agent's features such as inertia, effective temperature, quantum coherence, and quantum correlations with the receiver directly influence the work FTs. In any case, the BK formula is retrieved for very massive agents. Finally, we showed that the usually adopted TPM protocol is unable to capture the influence of entanglement to work FTs.

It would be interesting to further explore the work observable formalism in other autonomous systems and time intervals. As shown here, it allows us to dig deeper into the extension of FTs to more quantum regimes, specially within a fundamentally mechanical perspective. Moreover, we hope that some of the predictions made here can be experimentally tested in near future in the promising trapped ion platforms [149, 150].

7 Useful quantum mechanical work

The definitions of work derived from statistical physics, classical stochastic thermodynamics and quantum thermodynamics are constructed in order to capture the useful, trackable, deterministic and controllable character of a thermodynamic notion of work. The approaches seen in the quantum-thermodynamic context proved to be promising, being considered for increasingly general systems. However, as we saw in the Chapter 2, the definitions usually employed in quantum thermodynamics can lead to inconsistent results when considering autonomous systems with few particles, in which heat or work reservoirs are not trivially identifiable, and no thermal distributions or other usual thermodynamic assumptions are considered. Although it can be said that these definitions were not built for this class of systems, we can nevertheless try to construct a definition of work that has this trackable and useful thermodynamic character and that can be used in general autonomous systems, such as, few-particle, strongly interacting systems, for instance. In this chapter, we discuss our proposition of useful quantum mechanical (UQM) work which has a similar form to the physical-statistical formulation and can be used for a fairly general class of autonomous and non-autonomous systems.

Before presenting our definition, we will establish a mathematical definition of non-Fluctuating variables (NFVs, discussed in Chapter 2) and change it slightly so that it can be used in autonomous cases. With these definitions established, we can introduce our approach.

7.1 NFVs and ϵ-FVs

As set out in the Section 2.2, physical-statistical work, defined as

$$\delta\mathcal{W}_{\mathrm{sp}} = \partial_\lambda \langle H(\lambda)\rangle \, d\lambda, \tag{7.1}$$

seeks to capture the thermodynamic essence, establishing a trackable character related to the variable λ. These variables, which we call NFVs, shall not fluctuate in order to satisfy the Tolman criterion (criterion 1).

Since we want to obtain a definition of work in the form of Eq. (7.1) for quantum systems evolving unitarily, we must formally characterize the NFVs. For this, we consider again the systems described in the previous chapters: a system of interest S interacting with an environment E, whose $\mathrm{S}+\mathrm{E}$ initial state is represented by the density operator ρ; the system as a whole evolves unitarily U_t and we use the Heisenberg formalism with the same notations as before. Here, however, U_t may describe an autonomous (time-independent) or non-autonomous (time-dependent) process. Also, we denote any physical property of the system of interest S as $\mathscr{A}$, described mathematically by a Heisenberg (Hermitian) operator

A, at a given instant of time t. $\mathscr{A}$ can be taken, for example, as the position of a particle $\mathscr{X}$, with the respective position operator X.

In order for us to strictly associate a NFV to $\mathscr{A}$ consistent with Tolman's criterion, we must require that $\mathscr{A}$ does not fluctuate. Formally, it is necessary that

$$\sigma_A \equiv \sqrt{\langle (A(t) - \langle A(t) \rangle)^2 \rangle} \equiv \sqrt{\langle (\delta A(t))^2 \rangle}, \tag{7.2}$$

where we used the notation $\delta A(t) := A(t) - \langle A(t) \rangle$, adopted hereafter. Once the condition (7.2) is satisfied for a given interval $t \in [t_1, t_2]$, we can argue that $\langle A \rangle$ is a NFV in that interval, since the property $\mathscr{A}$ has no fluctuation (small variance) and $\langle A \rangle$ describes the value of this property. For example, if $\mathscr{A}$ is the position of a particular particle $\mathscr{X}$ and the corresponding operator X satisfies Eq. (7.2), we expect that in all measurements of the position $\mathscr{X}$, the result obtained will be $\langle X \rangle$, taken as a NFV. In general, we define NFVs strictly following Tolman's criterion:

Definition 7.1. *(NFVs) Consider a Hermitian operator A referring to the property $\mathscr{A}$ of the system of interest* S*. A Non-Fluctuating variable (NFV) $\langle A \rangle$ can be assigned to $\mathscr{A}$ during an interval $[t_1, t_2]$ if and only if A satisfies*

$$\sigma_A = 0 \tag{7.3}$$

during that interval.

This definition can be directly applied to non-autonomous systems, where explicitly time-dependent functions $\lambda(t)$ are assigned to a physical property. Indeed, $\lambda(t)$ can induce operators $\lambda(t)\mathbb{1}$ with null fluctuations, so that $\lambda(t)$ is precisely defined as a NFV.

By looking at Eq. (7.3), one can question its applicability in the autonomous quantum context, as we rarely expect in quantum systems that the variance of a given operator is zero and strictly satisfies the definition of NFV. For instance, consider the three-particle system described in Chapter 2, whose Hamiltonian is written as $H = \sum_{i=1}^{3} P_i^2/2m_i + \sum_{j>i=1}^{3} V_{ij}\left(X_i - X_j\right)$. In this case, for general states, the fluctuations associated with the position or velocity of one of the particles are not expected to be zero, so a NFV cannot be linked to these properties.

Another example is the the gas + piston + flame system, of which some microstates have been represented in Fig. 2.3 previously. We can consider our property of interest to be the position of the center of mass of the piston $\mathscr{X}_{\text{cm}}$ in relation to a frame of reference attached to the box that confines the gas; the operator that mathematically describes this property is the Hermitian position operator of the center of mass X_{cm}. If we measure $\mathscr{X}_{\text{cm}}$ and get the value L at any instant t, and compare with the mean $\langle X_{\text{cm}} \rangle$, resulting from several measurements obtained for the same process, we will see slight fluctuations in the position of the center of mass. This difference between a measured value and the average value, $L - \langle X_{\text{cm}} \rangle$ is highlighted in Fig. 7.1.

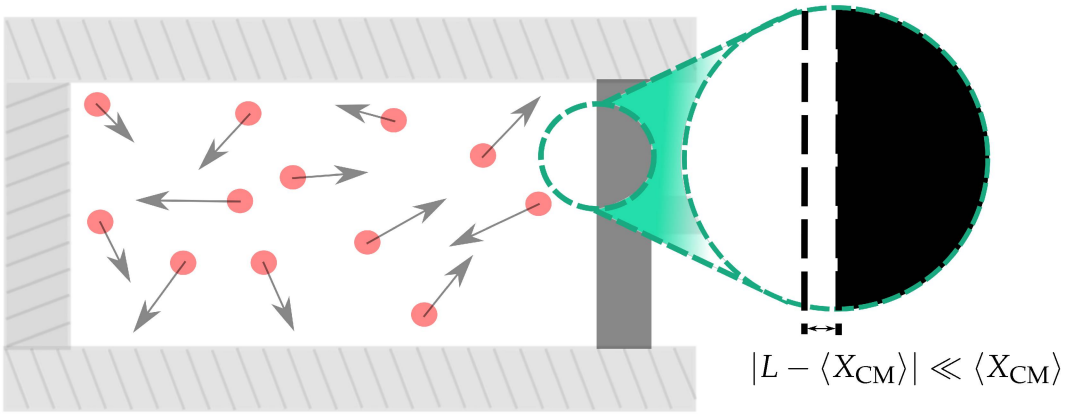


Figure 7.1 – Schematic representation of the measurement of the piston position at an instant t. Fluctuations can be seen when comparing the measurement result L and the average $\langle X_{\mathrm{cm}}\rangle$ obtained for several measurements made for the same procedure. When compared with the dimensions of the piston and the devices used in conjunction with it, these fluctuations are negligible. So it is approximately a NFV.

These two systems explain the fact that fluctuations are often present in autonomous systems, so we have to adapt the NFVs definition to them. We thus emphasize here another important aspect of the two examples mentioned above: although fluctuations for a given property are often present, they can be considered small when compared to certain scaling factors of the same property. For instance, if we assume that the displacement of the piston (of a particle) has an order of magnitude given in centimeters (micrometers), then fluctuations in position in micrometers will be negligible (relevant). In fact, macroscopic properties of many-particle systems, such as the piston's center of mass, are expected to have low fluctuations when compared to the relevant scales of the same properties[1], while fluctuations are generally significant and eventually dominant in smaller systems with fewer particles, as predicted by stochastic thermodynamics.

In general, we can associate to a physical property $\mathscr{A}$ an associated scale term $s_{\mathscr{A}}$, which represents the relevant order of magnitude of this same property. For example, if the displacement of the piston in Fig. 7.1 is of the order of centimeters, we have the scale factor $s_{\mathscr{X}_{\mathrm{cm}}} = 1\,\mathrm{cm}$, i.e. the relevant scale is given in centimeters.

Aiming to adapt the concept of NFV for autonomous systems for cases where fluctuations are not necessarily zero, we propose the definition of the ϵ-Fluctuating Variables (ϵFVs) and ϵ-Fluctuating Observables (OϵFs) as follows:

Definition 7.2. *(ϵ-FVs and ϵ-FOs) A property $\mathscr{A}$ of* S*, described mathematically by the*

[1] It is often assumed, in the physical-statistical description, that the energy and/or other macroscopic properties of a system constituted of a great number N of particles have little fluctuation when compared to the averages of these quantities. Approximately, this ratio is on the order of $1/\sqrt{N}$ [18, 40].

Hermitian operator A, is ϵ-Fluctuating at an instant t if and only if A satisfies

$$\frac{\sigma_A}{s_{\mathscr{A}}} \leq \epsilon \tag{7.4}$$

where ϵ is a finite dimensionless real number and $s_{\mathscr{A}}$ is a scaling factor (real and positive) accounting for the relevant orders of magnitude of the physical property $\mathscr{A}$. Accordingly, we call $\langle A \rangle$ and A the ϵ-Fluctuating Variable (ϵ-FV) and the ϵ-Fluctuating Observable (ϵ-FO), respectively.

Therefore, when $\epsilon \to 0$, a ϵ-FV converges to a NFV. Unlike NFVs, ϵ-FVs can be used in autonomous as well as non-autonomous systems, accounting for the practical fact that fluctuations are virtually always expected. In this sense, even though a control variable or a protocol is not imposed on the system, there may still be properties with negligible fluctuations, so that ϵ of a ϵ-FV tends to zero. Generally, $s_{\mathscr{A}}$ establishes what we accept as small for the physical property $\mathscr{A}$ so that its variance must not be exactly null when describing a trackable property, but very small in comparison to $s_{\mathscr{A}}$.

If we take the piston+gas+flame system described earlier in Fig. 7.1, the position of the center of mass $\mathscr{X}_{\mathrm{cm}}$ may be a ϵ-FV, with ϵ very small, so that $\langle X_{\mathrm{cm}} \rangle$ approaches an NFV, even though *we haven't assigned/enforced an explicit temporal dependency on this property*. The variance $\sigma_{\mathrm{X_{cm}}}$ is required to be significantly smaller than some scale $s_{\mathscr{X}_{\mathrm{cm}}}$ related to the center of mass. For example, in usual cases we can assume that the piston displacements are on the order of centimeters, so we assume $s_{\mathscr{X}_{\mathrm{cm}}} := 1\,\mathrm{cm}$. If the fluctuations are of the order of micrometers, then $\langle X_{\mathrm{cm}} \rangle$ is a ϵ-FV, with $\epsilon \approx 10^{-4}$; in some occasions, these values are enough to assume $\epsilon \approx 0$ and take $\langle X_{\mathrm{cm}} \rangle$ as a NFV.

As discussed in Chapter 2, the definition of work $\mathcal{W}_{\mathrm{sp}}$ coming from statistical physics is intricately connected to NFVs and therefore captures the useful, trackable character associated with thermodynamic work. Since we are looking for an analogous definition in an autonomous quantum context and possibly with few particles, our strategy is to adapt $\mathcal{W}_{\mathrm{sp}}$ regarding ϵ-FVs instead of NFVs. In the next section, we analyze in detail a simple example, in order to get some intuition on how such adaptation may take place.

7.2 Three particle system

Consider the three-particle case presented in Chapter 2, described in a quantum context by the non-autonomous Hamiltonian operator

$$H_{eff}(t) = \sum_{i=1}^{2} \frac{P_i^2}{2m_i} + V_{12}(X_1 - X_2) + V_{23}(X_2 - \lambda(t)), \tag{7.5}$$

as the quantum analogue of the classical Hamiltonian (Eq. (2.29)), where an explicitly time-dependent protocol $\lambda(t)$ is imposed to the position of particle 3.

Let us take the system of interest S as particles 2 and 3. Following the prescription of Chapter 3, their internal energy operator must be $E_{\mathrm{S}} = K_2 + K_3 + V_{23}$, where K_i are the kinetic energy operators. However, as considered in the construction of the classical Hamiltonian analogous to Eq. (7.5) (Eq. (2.29)), the kinetic energy associated with particle 3 is often disregarded, so that[2] $E_{\mathrm{S}} \approx K_2 + V_{23}(t)$. Taking its time derivative, we deduce

$$\frac{d}{dt}\left(K_2 + V_{23}(t)\right) = \mathcal{L}_{X_2}\left(\dot{X}_2\right) + \mathcal{L}_{\lambda}\left(\dot{\lambda}\right) \tag{7.6}$$

where the superoperators $\mathcal{L}_{X_2}(\cdot)$ and $\mathcal{L}_{\lambda}(\cdot)$ are defined as

$$\mathcal{L}_{X_2}\left(\dot{X}_2\right) = -\frac{1}{2}\left\{\partial_{X_2} V_{12}, \dot{X}_2\right\} \quad \text{e} \quad \mathcal{L}_{\lambda}\left(\dot{\lambda}\right) = \partial_{\lambda} V_{23}\dot{\lambda}. \tag{7.7}$$

The right-hand side of Eq. (7.6) can be seen as the quantum analogue of the classical chain rule: in this case, the term $\mathcal{L}_{X_2}\left(\dot{X}_2\right)$ can be seen as the quantum analogue of $(\partial_{X_2} H_{\mathrm{S}})\dot{X}_2$; in the special case of the classical variable $\mathcal{L}_{\lambda}\left(\dot{\lambda}\right)$ is in fact $(\partial_{\lambda} H_{\mathrm{S}})\dot{\lambda}$.

The mean value of the quantum mechanical work done on S in a short interval dt can be taken as

$$\langle \delta W_{\mathrm{E}\to\mathrm{S}} \rangle \equiv \langle W_{\mathrm{E}\to\mathrm{S}}(t+dt, t) \rangle = \left[\langle \mathcal{L}_{X_2}\left(\dot{X}_2\right)\rangle + \langle \mathcal{L}_{\lambda}\left(\dot{\lambda}\right)\rangle\right] dt = d\langle E_{\mathrm{S}} \rangle . \tag{7.8}$$

where the mean values $\langle \mathcal{L}_{X_2}\left(\dot{X}_2\right)\rangle$ and $\langle \mathcal{L}_{\lambda}\left(\dot{\lambda}\right)\rangle$ are taken with respect to time t. On the other hand, from a usual quantum thermodynamics perspective, the Hamiltonian Based (HB) definition (see Section 2.3) gives us

$$\delta W_{\mathrm{hb}} = \langle \partial_t H_{\mathrm{S}}(t) \rangle \, dt = \langle \mathcal{L}_{\lambda}\left(\dot{\lambda}\right)\rangle \, dt = f_{\lambda} d\lambda, \tag{7.9}$$

where $f_{\lambda} = \langle \mathcal{L}_{\lambda}\left(\dot{\lambda}\right)\rangle$ and $d\lambda = \dot{\lambda} dt$. Given that

$$\frac{d\langle E_{\mathrm{S}} \rangle}{dt} = \mathrm{Tr}_{\mathrm{S}}(\dot{\rho}_{\mathrm{S}}(t)(K_2^{\mathrm{s}} + V_{23}^{\mathrm{s}}(t))) + \langle \partial_{\lambda} V_{23}\dot{\lambda} \rangle \tag{7.10}$$

where $\dot{\rho}_{\mathrm{S}}(t) = \frac{d}{dt}\mathrm{Tr}_{\mathrm{E}}\left[U_t \rho U_t^{\dagger}\right]$, we obtain, comparing Eq. (7.10) with Eq. (7.6), that

$$\langle \mathcal{L}_{X_2}\left(\dot{X}_2\right)\rangle \, dt = \mathrm{Tr}_{\mathrm{S}}\left[\dot{\rho}_{\mathrm{S}}(t)\left(K_2^{\mathrm{s}} + V_{23}^{\mathrm{s}}(t)\right)\right] dt \equiv \delta Q_{\mathrm{hb}} \tag{7.11}$$

is the HB heat. As a consequence, we have that

$$d\langle E_{\mathrm{S}} \rangle = \langle \delta W_{\mathrm{E}\to\mathrm{S}} \rangle = \delta W_{\mathrm{hb}} + \delta Q_{\mathrm{hb}}. \tag{7.12}$$

Up to this point, we derive results obtained solely from the definition of QM work and HB work and heat. However, as we asked earlier in the Section 2.4, what would happen if a property, say the position of particle 2, had extremely small fluctuations? Would this variable induce another form of work similar to the physical-statistical form?

[2] Note that this form "emulates" the inclusive formulation. However, the meaning here is different, as our system of interest is now taken as particles 2 and 3 rather than just particle 2.

We tackle this questioning by equipping ourselves with the ϵ-FVs, defined in the previous section. From the start, the position of particle 3 described by the variable $\lambda(t)$ is an NFV and therefore a 0-FV. Thus, $\delta W_{\rm hb}$ has a form similar to physical-statistical work $\delta \mathcal{W}_{\rm sp}$, as expected.

Let us assume now that X_2 as well as $\dot{X}_2$ are ϵ-FOs, i.e., that for any $t \in [t_1, t_2]$,

$$\frac{\sigma_{X_2}}{s_{\mathscr{X}_2}} \leq \epsilon, \quad \text{and} \quad \frac{\sigma_{\dot{X}_2}}{s_{\dot{\mathscr{X}}_2}} \leq \epsilon, \tag{7.13}$$

where the scale factors can be assumed to be the "average displacement" in the interval $[t_1, t_2]$, $s_{\mathscr{X}_2} = (t_2 - t_1)^{-1} \int_{t_1}^{t_2} |\langle \dot{X}_2(t) \rangle| \, dt$, and the average speed $s_{\dot{\mathscr{X}}_2} = |\langle \dot{X}_2 \rangle|$. Given the operator $\delta \dot{X}_2 = \dot{X}_2 - \langle \dot{X}_2 \rangle$, then $\mathcal{L}_{X_2}\left(\dot{X}_2\right)$, defined in Eq. (7.7), can be rewritten as

$$\begin{aligned} \mathcal{L}_{X_2}(\dot{X}_2) &= -\tfrac{1}{2}\left\{\partial_{X_2} V_{12}, \dot{X}_2\right\} = -\tfrac{1}{2}\left\{\partial_{X_2} V_{12}, \langle \dot{X}_2 \rangle\right\} - \tfrac{1}{2}\left\{\partial_{X_2} V_{12}, \delta \dot{X}_2\right\} \\ &= \mathcal{L}_{X_2}(\mathbb{1}) \langle \dot{X}_2 \rangle + \mathcal{L}_{X_2}(\delta \dot{X}_2). \end{aligned} \tag{7.14}$$

From the Cauchy-Schwartz inequality, we can deduce that

$$|\langle \mathcal{L}_{X_2}(\delta \dot{X}_2) \rangle| \leq \sqrt{\langle \delta^2 \dot{X}_2 \rangle} \sqrt{\langle (\partial_{X_2} V_{12})^2 \rangle} = \sigma_{\dot{X}_2} \sqrt{\langle (\partial_{X_2} V_{12})^2 \rangle} \tag{7.15}$$

so that, from Eq. (7.13), it follows that

$$|\langle \mathcal{L}_{X_2}(\delta \dot{X}_2) \rangle| \leq \epsilon |\langle \dot{X}_2 \rangle| \sqrt{\langle (\partial_{X_2} V_{12})^2 \rangle} \tag{7.16}$$

As a result, if both $\sqrt{\langle (\partial_{X_2} V_{12})^2 \rangle}$ and $|\langle \dot{X}_2 \rangle|$ are bounded and ϵ is sufficiently small, then $|\langle \mathcal{L}_{X_2}(\delta \dot{X}_2) \rangle| \approx 0$, so that

$$\langle \mathcal{L}_{X_2}(\dot{X}_2) \rangle \approx \mathcal{L}_{X_2}(\mathbb{1}) \langle \dot{X}_2 \rangle = -\langle \partial_{X_2} V_{12} \rangle \langle \dot{X}_2 \rangle \tag{7.17}$$

and we can write

$$\langle \mathcal{L}_{X_2}\left(\dot{X}_2\right) \rangle \, dt \approx f_{x_2} dx_2 \tag{7.18}$$

with $f_{X_2} = -\langle \partial_{X_2} V_{12} \rangle$ and $x_2 = \langle X_2 \rangle$, $dx_2 = \langle \dot{X}_2 \rangle \, dt$.

Therefore, when ϵ is small enough not only $\langle X_2 \rangle$ behaves similarly to a NFV but it also induces a form of work, $f_{x_2} dx_2$, similar to the definition $\delta \mathcal{W}_{\rm sp}$ coming from statistical physics. Note that while $\langle X_2 \rangle$ is not an *external* variable, in the sense of having an explicit time dependency *imposed* on it, it can be taken as a NFV for sufficiently small fluctuations (*a la* Tolman's criterion).

Although $f_{x_2} dx_2$ has a similar form as $\delta W_{\rm sp}$, it was not deduced in a context where usual hypotheses of statistical physics are assumed, such as equilibrium, thermal baths, among others. Even so, it captures, together with $f_\lambda d\lambda$, the deterministic essence of thermodynamics work, since *we can link a variable that evolves approximately deterministically to the energy transfer to a given system* S. Considering Eqs. (7.6), (7.9) and (7.18) we have that Eq. (7.12) can be rewritten, for any small interval $[t, t + dt] \subset [t_1, t_2]$, as

$$dE_{\rm S} \approx \delta W_{\rm u} = f_{x_2} dx_2 + f_\lambda d\lambda \tag{7.19}$$

where we defined δW_{u} as the *useful quantum-mechanical* UQM work: it takes into account the NFV λ of the system and the ϵ-FV $\langle X_2 \rangle$ with relatively small fluctuations ϵ, in order to account for a useful, predictable form of transference of energy, analogous to $\delta \mathcal{W}_{\mathrm{sp}}$.

By comparing Eq. (7.11) with Eq. (7.19), we notice that $f_{x_2} dx_2$ is taken as HB heat in the former equation, while UQM work in the latter. As we argued in Section 2.4, δW_{u} captures essential features of thermodynamic work, since the predictable, trackable, and low-fluctuation nature of $\langle X_2 \rangle$ is taken into account. It does not seem physically consistent to call $f_{x_2} dx_2$ heat in such a context.

It is worth emphasizing here that δW_{u} is developed here in a mechanical context, where we do not necessarily demand thermal baths, distributions in equilibrium, among other hypotheses used in the Statistical Physics context. Here, it is only necessary that Eq. (7.13) to be satisfied, for ϵ with a sufficiently small value. Furthermore, with these conditions satisfied, nothing prevents us from identifying UQM work in the form $f_{x_2} dx_2$ for a fully autonomous dynamics case, i.e., where a function $\lambda(t)$ is not imposed on the position of particle 3 and the Hamiltonian is described by

$$H = \sum_{i=1}^{3} \frac{P_i^2}{2m_i} + \sum_{i<j} V_{ij}(X_i - X_j). \tag{7.20}$$

Still, we can consider other systems of interest and other properties: if we identify ϵ-FOs with low values for ϵ, then we can construct other forms of UQM work. In fact, in the sequence, we expanded the results of this section to a sufficiently general class of systems.

7.3 UQM work: more general systems

Aiming at consistently generalizing the notion of UQM work described in the previous section, we consider here internal energy operators E_{S} that meet the internal energy criterion described in Chapter 3 and satisfy the following hypotheses for any instant of time of a given interval $[t_1, t_2]$:

- (H1) $E_{\mathrm{S}}^{\mathrm{s}}$, i.e. the Schrödinger version of E_{S}, can be explicitly time-dependent and we will impose that for every instant, its Heisenberg version can be written as a sum of powers of a family of N Heisenberg Hermitian operators $\{A_i\}_{i=1}^{N}$ in the form

$$E_{\mathrm{S}} = \sum_{i,j=1}^{N} \sum_{n_i, n_j} c_{ij}^{n_i n_j} A_i^{n_i} A_j^{n_j}, \tag{7.21}$$

  where $c_{ij}^{n_i n_j}$ are time-independent scalars. In non-autonomous cases, where $H_{\mathrm{S}}^{\mathrm{s}}$ is described in terms of controlled variables λ_i, then these induce Hermitian operators $A_\lambda = \lambda_i \mathbb{1}$ that are included in the family $(A_i)_{i=1}^{N}$; we assume that *the time-dependent operators are only described in this form*;

- (H2) The operators in (7.21) are bounded so that there are real constants C_{ij}, such that

$$\langle (A_i^{n_i} A_j^{n_j})^\dagger (A_i^{n_i} A_j^{n_j}) \rangle \leq C_{ij} \tag{7.22}$$

and, additionally, we demand that for any $k \leq m_i \leq n_i$ and $m_j \leq n_j$, there are real constants C'_{m_i,m_j} such that

$$\langle (A_i^{m_i-k} \dot{A}_i A_i^k A_j^{m_j})^\dagger (A_i^{m_i-k} \dot{A}_i A_i^k A_j^{m_j}) \rangle \leq C'_{m_i,m_j} \tag{7.23}$$

and

$$\langle (A_i^{m_i} A_j^{m_j-k} \dot{A}_j A_j^k)^\dagger (A_i^{m_i} A_j^{m_j-k} \dot{A}_j A_j^k) \rangle \leq C'_{m_i,m_j}. \tag{7.24}$$

We also assume that the coefficients tend to zero as the powers increase, i.e. $|c_{ij}^{n_i n_j}| \to 0$ when $n_i \to \infty$ or $n_j \to \infty$.

We chose the form (7.21) since it is suitable for a general class of systems and allows a more direct deduction of the results to be presented. As an example, we may consider the N particle system discussed in Chapter 3, described by the Hamiltonian

$$H = \sum_{i=1}^{N} \frac{P_i^2}{2m_i} + \sum_{j>i=1}^{N} V_{ij}\left(X_i - X_j\right). \tag{7.25}$$

By selecting the first M particles as our system of interest S, E_S is therefore taken as

$$E_S = \sum_{i=1}^{M} \frac{m_i \dot{X}_i^2}{2} + \sum_{j>i,i=1}^{M} V_{ij}\left(X_i - X_j\right) \tag{7.26}$$

which, can be written in the form (7.21), in terms of operators of the family $(\dot{X}_i, X_i)_{i=1}^M$. Among other examples with the form (7.21), we can mention the Jaynnes-Cummings model [151] or the Caldeira-Leggett model [102].

It is important to highlight here that the same internal energy operator can be written in many different ways. For instance, in the case of the M particles in Eq. (7.21), we can write the internal energy in the alternative form

$$E_S = \sum_{i=1}^{M} \frac{P_i^2}{2m_i} + \sum_{j>i,i=1}^{M} V_{ij}\left(X_i - X_j\right) \tag{7.27}$$

In this case, the family of operators that defines E_S is $(P_i, X_i)_{i=1}^M$, unlike $(\dot{X}_i, X_i)_{i=1}^M$. We could consider still other ways of writing E_S, in terms of different families of operators. To simplify the analysis, the Hermitian operators A_i that we choose to describe the internal energy operator in the form (7.21) will be called *relevant operators* and the physical properties attached to them, $\mathscr{A}_i$, are called *relevant properties*. Therefore, if E_S of the system of M particles is written as in Eq. (7.26)/(7.27), then the relevant operators shall be $(\dot{X}_i, X_i)_{i=1}^M$/$(P_i, X_i)_{i=1}^M$.

Hypothesis (H2) is strongly dependent on the state and evolution of the system. In general, (H2) will be satisfied for finite discrete systems. If we consider continuous systems,

however, the results to be presented in the sequence are valid only if the density operator is "well-behaved" so that the conditions (7.22), (7.23) and (7.24) are met.

From this moment on, we will assume that (H1) and (H2) are satisfied. As a consequence, the temporal derivative of the operator H_{S} (7.21) can then be written as

$$\dot{H}_{\mathrm{S}} = \sum_{j=1}^{N} \mathcal{L}_j\left(\dot{A}_j\right) \tag{7.28}$$

with $\mathcal{L}_j\left(\cdot\right)$ denoting linear superoperators acting in operator space, written as

$$\begin{aligned} \mathcal{L}_j\left(\dot{A}_j\right) &= \textstyle\sum_{i=1}^{N}\sum_{n_i,n_j} c_{ij}^{n_i n_j} A_i^{n_i}\left(\sum_{k=0}^{n_j-1} A_j^{k}\left(\dot{A}_j\right) A_j^{n_j-k-1}\right) \\ &+ \textstyle\sum_{l=1}^{N}\sum_{n_j,n_l} c_{jl}^{n_j n_l}\left(\sum_{k=0}^{n_j-1} A_j^{k}\left(\dot{A}_j\right) A_j^{n_j-k-1}\right) A_l^{n_l}. \end{aligned} \tag{7.29}$$

As in the previous section, the right-hand side of Eq. (7.28) can be seen as the "quantum chain rule", with $\mathcal{L}_{A_j}\left(\dot{A}_j\right)$ as the quantum analogues of $\left(\partial_{A_j} H_{\mathrm{S}}\right)\dot{A}_j$.

Now, if some of the operators A_i, with $i \in \mathfrak{C}$ and $\mathfrak{C} \subset [1, 2\cdots, N]$, are replaced by their averages in the expression (7.28), i.e. $A_i \to \langle A_i\rangle\,\mathbb{1}$ in (7.28), then the new energy operator resulting from such a substitution is denoted as $H_{\mathrm{S}}^{\mathfrak{C}}$. Its time derivative can be deduced to be (see Eq. (D.5) from Appendix D)

$$\dot{H}_{\mathrm{S}}^{\mathfrak{C}} = \sum_{j\in\mathfrak{C}} \mathcal{L}_j^{\mathfrak{C}}\left(\partial_t\langle A_j\rangle\mathbb{1}\right) + \sum_{j\notin\mathfrak{C}} \mathcal{L}_j^{\mathfrak{C}}\left(\dot{A}_j\right) \tag{7.30}$$

where $\mathcal{L}_j^{\mathfrak{C}}$ are the superoperators resultant from the replacement $A_i \to \langle A_i\rangle\,\mathbb{1}$, $i \in \mathfrak{C}$, in Eq. (7.29). With these considerations and notations in mind, we prove, in Appendix D, the following theorem:

Theorem 7.1. *If (H1) and (H2) are satisfied and if, for all $j \in \mathfrak{E}$ in a given index set $\mathfrak{E} \subset [1, 2\cdots, N]$, A_j and $\dot{A}_j$ are ϵ-FOs, i.e.,*

$$\frac{\sigma_{A_j}}{s_{\mathscr{A}_j}} \leq \epsilon, \quad \textit{and} \quad \frac{\sigma_{\dot{A}_j}}{s_{\dot{\mathscr{A}}_j}} \leq \epsilon, \tag{7.31}$$

then

$$\left|\,\langle\dot{E}_{\mathrm{S}}\rangle - \langle\dot{E}_{\mathrm{S}}^{\mathfrak{E}}\rangle\,\right| \leq C\epsilon \tag{7.32}$$

where C is a real, positive, bounded constant. Consequently, if $\epsilon \to 0$, then $\langle\dot{E}_{\mathrm{S}}\rangle \to \langle\dot{E}_{\mathrm{S}}^{\mathfrak{E}}\rangle$. We call the set of indices $\mathfrak{E}$ the ϵ-Fluctuating Set.

This theorem shows that if the physical properties $\mathscr{A}_j$ and $\dot{\mathscr{A}}_j$ of S have close-to-zero fluctuations compared to the scale factors $s_{\mathscr{A}_j}$ and $s_{\dot{\mathscr{A}}_j}$, then the average values of the corresponding operators A_j and $\dot{A}_j$ behave as NFVs, and, from the result (7.32),

$$\langle\dot{E}_{\mathrm{S}}\rangle \approx \langle\dot{E}_{\mathrm{S}}^{\mathfrak{E}}\rangle = \sum_{j\notin\mathfrak{E}}\langle\mathcal{L}_j^{\mathfrak{E}}(\dot{A}_j)\rangle + \sum_{j\in\mathfrak{E}}\langle\mathcal{L}_j^{\mathfrak{E}}(\mathbb{1})\rangle\,\langle\dot{A}_j\rangle\,. \tag{7.33}$$

The example of the three particles, presented in the previous section, is a special case of the Theorem 7.1: if we take particles 2 and 3 as our internal system, then $\langle \dot{E}_{\mathrm{S}} \rangle = \langle \mathcal{L}_{X_2}(\dot{X}_2) \rangle + \langle \mathcal{L}_{\lambda}(\dot{\lambda}) \rangle$ (Eq. (7.6)) and, when the position and velocity of particle 2 have extremely small fluctuations, then $\langle \dot{E}_{\mathrm{S}} \rangle \approx \langle \dot{E}_{\mathrm{S}}^{\mathfrak{E}} \rangle = \langle \mathcal{L}_{X_2}^{\mathfrak{E}}(\mathbb{1}) \rangle \langle X_2 \rangle + \langle \mathcal{L}_{\lambda}^{\mathfrak{E}}(\dot{\lambda}) \rangle$, where we replace $X_2 \to \langle X_2 \rangle \mathbb{1}$.

In the example of the three particles, we defined the UQM work represented in Eq. (7.18). Likewise, for the more general case E_{S}, described in Eq. (7.21), we can define the UQM work for any interval $[t, t+dt] \subset [t_1, t_2]$ in a more general context as

$$\delta W_{\mathrm{u}} := \sum_{j \in \mathfrak{E}} \langle \mathcal{L}_j^{\mathfrak{E}} \left(\langle \dot{A}_j \rangle \mathbb{1} \right) \rangle \, dt \equiv \sum_{j \in \mathfrak{E}} \langle \mathcal{L}_j^{\mathfrak{E}} \left(\mathbb{1} \right) \rangle \langle \dot{A}_j \rangle \, dt \tag{7.34}$$

such that

$$d \langle E_{\mathrm{S}} \rangle := \langle \dot{E}_{\mathrm{S}} \rangle \, dt = \langle \delta W_{\mathrm{E} \to \mathrm{S}} \rangle \approx \delta W_{\mathrm{u}} + \sum_{j \notin \mathfrak{E}} \left\langle \mathcal{L}_j^{\mathfrak{E}} \left(\dot{A}_j \right) \right\rangle . \tag{7.35}$$

Therefore, if the system as a whole is autonomous and some observables A_i, $i \in \mathfrak{E}$ have sufficiently small fluctuations, then *it is still possible to define a work in a form similar to the statistical physics* $f_{a_i} da_i$, *with* $f_{a_i} = \langle \mathcal{L}_i^{\mathfrak{E}} (\mathbb{1}) \rangle$ *and* $da_i = \langle \dot{A}_i \rangle dt$. This work, as mentioned before, allows us to obtain a useful, trackable form of energy transfer, in the sense that we can link to this transfer a variable of low dispersion, predictable, semi-classical. Note that, unlike the non-autonomous case, the dynamics of the variables that define UQM work can be a consequence of the unitary evolution of the system as a whole and not an imposed dynamics. Furthermore, the form (7.34) covers both non-autonomous systems and autonomous systems with low fluctuation operators: the family of operators $(A_i)_{i \in \mathfrak{E}}$ can be constituted by 0-FOs induced by externally imposed functions λ_i in non-autonomous scenarios and/or ϵ-FOs, with sufficiently small ϵ.

When looking at Eq. (7.35), and taking into account the first law of thermodynamics, we are tempted to define $d \langle E_{\mathrm{S}} \rangle - \delta W_{\mathrm{u}}$ as heat. Indeed, we expect that the heat transfer is accompanied by non-negligible fluctuations. In this direction, we aim to show now that δW_{u} and $d \langle E_{\mathrm{S}} \rangle - \delta W_{\mathrm{u}}$ at a very specific limit converges to the usual work and heat definitions for non-autonomous systems and have an analogous correspondence in a class of autonomous systems.

We first note that the operator $E_{\mathrm{S}}^{\mathfrak{E}}$ will usually have its Schrödinger version $[E_{\mathrm{S}}^{\mathfrak{E}}]^{\mathfrak{s}} = U_t E_{\mathrm{S}}^{\mathfrak{E}} U_t^{\dagger}$ explicitly time dependent (see Eq. (D.41) from Appendix D). Furthermore, as in the usual cases of non-autonomous systems, if we additionally assume that $(H_{\mathrm{S}}^{\mathfrak{E}})^{\mathfrak{s}}$ acts only on the Hilbert space of the system of interest $\mathbb{H}_{\mathrm{S}}$, then we get the following corollary of Theorem 7.1:

Corollary 7.1. *Considering the same hypotheses of Theorem 7.1 and that* $(E_{\mathrm{S}}^{\mathfrak{E}})^{\mathfrak{s}}$ *acts on the Hilbert space of the system of interest* $\mathbb{H}_{\mathrm{S}}$*, then*

$$\left| \langle \dot{E}_{\mathrm{S}} \rangle - \left(\mathrm{Tr}_{\mathrm{S}} \left[\rho_{\mathrm{S}}(t) \partial_t [E_{\mathrm{S}}^{\mathfrak{E}}]^{\mathfrak{s}} \right] + \mathrm{Tr}_{\mathrm{S}} \left[\partial_t \rho_{\mathrm{S}}(t) [E_{\mathrm{S}}^{\mathfrak{E}}]^{\mathfrak{s}} \right] \right) \right| \leq C\epsilon, \tag{7.36}$$

with

$$\sum_{j\in\mathfrak{E}}\langle\mathcal{L}_j^{a_{i\in\mathfrak{E}}}(\dot{a}_j)\rangle = \mathrm{Tr_S}\left[\rho_\mathrm{S}(t)\partial_t[E_\mathrm{S}^\mathfrak{E}]^\mathfrak{s}\right], \tag{7.37}$$

and

$$\sum_{j\notin\mathfrak{E}}\langle\mathcal{L}_j^{a_{i\in\mathfrak{E}}}(\dot{a}_j)\rangle = \mathrm{Tr_S}\left[\partial_t\rho_\mathrm{S}(t)[E_\mathrm{S}^\mathfrak{E}]^\mathfrak{s}\right], \tag{7.38}$$

where C is a real, positive and bounded constant and $\rho_\mathrm{S}(t)$ and $\mathrm{Tr_S}$ refer respectively to the reduced density operator and the trace of the reduced space. As a consequence,

$$\lim_{\epsilon\to 0}\langle\dot{E}_\mathrm{S}\rangle = \mathrm{Tr_S}\left[\rho_\mathrm{S}(t)\partial_t[E_\mathrm{S}^\mathfrak{E}]^\mathfrak{s}\right] + \mathrm{Tr_S}\left[\partial_t\rho_\mathrm{S}(t)[E_\mathrm{S}^\mathfrak{E}]^\mathfrak{s}\right]. \tag{7.39}$$

Therefore, if the Corollary hypotheses are satisfied, UQM work will have a similar form as HB work

$$\delta W_\mathrm{u} \approx \mathrm{Tr_S}\left[\rho_\mathrm{S}(t)\partial_t[E_\mathrm{S}^\mathfrak{E}]^\mathfrak{s}\right], \tag{7.40}$$

and the difference between the internal energy and UQM work will have a form very similar to the HB heat:

$$d\langle E_\mathrm{S}\rangle - \delta W_\mathrm{u} \approx \mathrm{Tr_S}\left[\partial_t\rho_\mathrm{S}(t)[E_\mathrm{S}^\mathfrak{E}]^\mathfrak{s}\right]. \tag{7.41}$$

Although these expressions are similar to the usual HB definitions of work $\delta W_\mathrm{hb} = \mathrm{Tr}[\rho_\mathrm{S}(t)\partial_t H(t)]$ and heat $\delta Q_\mathrm{hb} = \mathrm{Tr}[\partial_t\rho_\mathrm{S}(t)H(t)]$, respectively, the system here can be autonomous and, for the non-autonomous case, it may differ from HB definitions: although $E_\mathrm{S}^\mathfrak{E}$ has a similar form to a non-autonomous Hamiltonian $H(t)$, it is, however, the result of replacing some operators A_i by their average values $\langle A_i\rangle\mathbb{1}$; Unlike the externally controlled $\lambda(t)$, $\langle A_i\rangle$ have their temporal dependence generally dictated by the unitary evolution and not by an imposed, controlled protocol. However, *in cases where the only ϵ-FVs are the imposed functions $\lambda(t)$, then UQM work will converge to HB work and the difference $d\langle E_\mathrm{S}\rangle - \delta W_\mathrm{u}$ will be HB heat.*

Finally, we formulate the following "algorithm" to compute UQM work:

1. Determine the dynamics by solving the Schrödinger equation or Heisenberg equations for the relevant operators A_i;
2. Define the internal energy operator E_S and find, if possible, the related ϵ-FOs, with $\epsilon \ll 1$;
3. Determine the operators $E_\mathrm{S}^\mathfrak{E}$ and $\dot{E}_\mathrm{S}^\mathfrak{E}$ resultant from the replacement $A_{i\in\mathfrak{E}} \to \langle A_{i\in\mathfrak{E}}\rangle\mathbb{1}$ of the ϵ-FOs defined in the previous step;
4. If the hypotheses of Theorem 7.1 are satisfied, use the definition of UQM work (7.34); if, moreover, the system satisfies the assumptions of Corollary 7.1, UQM work can be computed from Eq. (7.40).

In the following section, we present an example in which we study the applicability of the definitions and results presented in this chapter.

7.4 Piston+Gas+Environment

Our aim here is to show how our definitions can be suitably applied to macroscopic systems. We do not intend here to solve the dynamics and obtain expressions for the state or the observables at a given time. Instead, we analyze how the conditions of fluctuations in some observables together with the definitions and results presented in the previous sections can result in known thermodynamic expressions consistent with the mechanical principles presented in Chapter 3 and without appealing to classic, controlled protocols.

The system we deal with is depicted in Fig. 7.2. A cat, that acts as a push/pull agent on the piston, together with an external gas and the container walls make up the outer system O. Inside the container, a gas G is confined by the piston P.

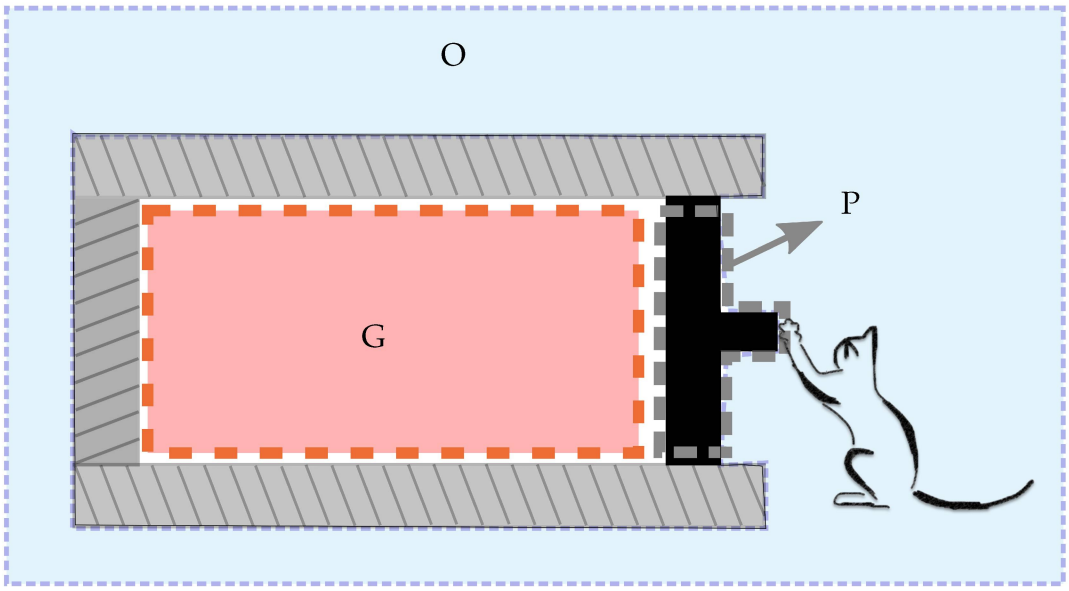


Figure 7.2 – Gas (G) confined by a piston (P). The cat pulling/pushing the piston together with an external gas and the container is considered the outer system (O). The entire $\mathrm{G}\cup\mathrm{P}\cup\mathrm{O}$ system is isolated and evolves autonomously through relative-position-dependent interactions.

We assume that the interactions between the particles are all in terms of relative position, so that the Hamiltonian operator of every system is described by

$$H = H_{\mathrm{G}} + V_{\mathrm{PG}} + H_{\mathrm{P}} + H_{\mathrm{I}} + H_{\mathrm{O}} \tag{7.42}$$

where

$$H_{\mathrm{G,P,O}} = \sum_{i\in\mathrm{G,P,O}} \frac{P_i^2}{2m_i} + \frac{1}{2}\sum_{i,j\in\mathrm{G,P,O}} V_{ij}\left(X_i - X_j\right), \tag{7.43}$$

refer to the internal energy of the gas, piston and external system, respectively, and the notations in the form $i \in \mathrm{G}$ indicate that the ith particle belongs to G and so on. We define the interaction terms as

$$V_{\mathrm{PG}} = \sum_{i\in\mathrm{G}}\sum_{j\in\mathrm{P}} V_{ij}\left(X_i - X_j\right) \tag{7.44}$$

accounting for the interaction between the gas with the piston and

$$H_{\mathrm{I}} = \sum_{i\in \mathrm{G}\cup\mathrm{P}} \sum_{j\in\mathrm{O}} V_{ij}\left(X_i - X_j\right) \tag{7.45}$$

describing the interaction between the gas and the piston with the system O (note that the union $\mathrm{G}\cup\mathrm{P}$ accounts for the gas and piston indices).

Let us take the piston and the gas as our system of interest S and, as previously described, the system O makes up the exterior $\mathrm{O}\equiv\mathrm{E}$. In accordance with Chapter 3, the internal energy operator is $E_{\mathrm{S}} \to H_{\mathrm{G}} + V_{\mathrm{PG}} + H_{\mathrm{P}}$. Moreover, the total QM work done on S during a short interval $[t, t+dt] \subset [t_1, t_2]$ can be computed as

$$dE_{\mathrm{S}} = \sum_{i\in\mathrm{G}\cup\mathrm{P}} \sum_{k\in\mathrm{E}} -\frac{1}{2}\{\partial_{\mathrm{X}_i} V_{ik}, \dot{X}_i\}dt = \sum_{i\in\mathrm{G}\cup\mathrm{P}} \sum_{k\in\mathrm{E}} \delta\mathcal{W}_{k\to i} = \delta\mathcal{W}_{\mathrm{E}\to\mathrm{S}}, \tag{7.46}$$

where $\delta\mathcal{W}_{k\to i} = -\frac{1}{2}\langle\{\partial_{\mathrm{X}_i} V_{ik}\left(X_i - X_k\right), \dot{X}_i\}\rangle\, dt'$ is the work done by the kth particle of the external system E on the ith particle of the system of interest $\mathrm{G}\cup\mathrm{P}\equiv\mathrm{S}$.

Given certain assumptions, we can compute a UQM work associated. First, we will change the piston coordinate system so that

$$X_{\mathrm{cm}} = \frac{\sum_{i\in\mathrm{P}} m_i X_i}{M_p} \quad \text{e} \quad P_{\mathrm{cm}} = \sum_{i\in\mathrm{P}} P_i, \tag{7.47}$$

are respectively the position and moment of the center of mass of the piston, with $M_{\mathrm{P}} = \sum_{i\in\mathrm{P}} m_i$ being the total mass of the piston, and

$$X_i^{\mathrm{r}} = X_i - X_{\mathrm{cm}} \quad \text{e} \quad P_i^{\mathrm{r}} = P_i - \frac{m_i}{M_p} P_{\mathrm{cm}} \tag{7.48}$$

are the relative coordinates. The average change in internal energy (and therefore QM work) during the interval $[t, t+dt]$ can then be rewritten in terms of this new coordinate system as

$$\langle\delta\mathcal{W}_{\mathrm{E}\to\mathrm{S}}\rangle = d\langle E_{\mathrm{S}}\rangle = \sum_{j\in\mathrm{G}} \langle\mathcal{L}_{\mathrm{X}_j}(\dot{X}_j)\rangle\, dt + \sum_{k\in\mathrm{P}} \langle\mathcal{L}_{X_k^{\mathrm{r}}}(\dot{X}_k^{\mathrm{r}})\rangle\, dt + \langle\mathcal{L}_{\mathrm{X}_{\mathrm{cm}}}(\dot{X}_{\mathrm{cm}})\rangle\, dt \tag{7.49}$$

where

$$\begin{aligned}
\mathcal{L}_{\mathrm{X}_j}(\cdot) &= -\textstyle\sum_{i\in\mathrm{E}} \frac{1}{2}\left\{\partial_{\mathrm{X}_j} V_{ij}\left(X_i - X_j\right), (\cdot)\right\} \\
\mathcal{L}_{X_k^{\mathrm{r}}}(\cdot) &= -\textstyle\sum_{i\in\mathrm{E}} \frac{1}{2}\left\{\partial_{\mathrm{X}_k} V_{ik}\left(X_i - (X_k^{\mathrm{r}} + X_{\mathrm{cm}})\right), (\cdot)\right\}, \\
\mathcal{L}_{\mathrm{X}_{\mathrm{cm}}}(\cdot) &= \textstyle\sum_{i\in\mathrm{E}, k\in\mathrm{P}} -\frac{1}{2}\left\{\partial_{\mathrm{X}_k} V_{ik}\left(X_i - (X_k^{\mathrm{r}} + X_{\mathrm{cm}})\right), (\cdot)\right\}.
\end{aligned} \tag{7.50}$$

Now, it is expected that the position and velocity of the center of mass have small fluctuation when compared to their average values. In fact, if we assume that the velocities of the piston N_{P} particles satisfy

$$\frac{\sum_{i\in\mathrm{P}} m_i \sigma_{\dot{X}_i}}{\sum_{i\in\mathrm{P}} m_i |\langle\dot{X}_i\rangle|} \leq \frac{1}{\sqrt{N_{\mathrm{P}}}}, \tag{7.51}$$

then it is possible to prove (Appendix E) that for a preparation with small initial fluctuations $\sigma_{\mathrm{X}_{\mathrm{cm}}}$ and $\sigma_{P_{\mathrm{cm}}}$, these fluctuations should still be small after a time interval. As a result, if these

conditions are satisfied, X_{cm} and P_{cm} can be taken as ϵ-FOs, with $\epsilon \ll 1$. In this sense, from Theorem 7.1, UQM work can be defined as[3]

$$\delta W_{\text{u}} = \langle \mathcal{L}^{\mathfrak{E}}_{X_{\text{cm}}}(\mathbb{1}) \rangle \langle \dot{X}_{\text{cm}} \rangle \, dt, \tag{7.52}$$

and

$$d\langle E_{\text{S}} \rangle - \delta W_{\text{u}} = \sum_{j \in \text{G}} \langle \mathcal{L}^{\mathfrak{E}}_{X_j}(\dot{X}_j) \rangle \, dt + \sum_{k \in \text{P}} \langle \mathcal{L}^{\mathfrak{E}}_{X^{\text{r}}_k}(\dot{X}^{\text{r}}_k) \rangle \, dt \tag{7.53}$$

where $\mathcal{L}^{\mathfrak{E}}_{X_j}$, $\mathcal{L}^{\mathfrak{E}}_{X^{\text{r}}_k}$ and $\mathcal{L}^{\mathfrak{E}}_{X_{\text{cm}}}$ results from the substitution $X_{\text{cm}} \to \langle X_{\text{cm}} \rangle$ in $\mathcal{L}_{X_j}$, $\mathcal{L}_{X^{\text{r}}_k}$, and $\mathcal{L}_{X_{\text{cm}}}$, respectively. From Eq. (7.52), we can see that the UQM work encapsulates macroscopic system effects, as $\langle \mathcal{L}^{\mathfrak{E}}_{X_{\text{cm}}}(\mathbb{1}) \rangle$ can be seen as the average force applied by the E system on the piston, defined as

$$\langle F_{\text{E}\to\text{P}} \rangle = \sum_{i \in \text{E}, k \in \text{P}} - \langle \partial_{X_k} V_{ik} \left(X_i - (X^{\text{r}}_k + X_{\text{cm}}) \right) \rangle \, . \tag{7.54}$$

Therefore $\delta W_{\text{u}} = \langle F_{\text{E}\to\text{P}} \rangle \langle \dot{X}_{\text{cm}} \rangle \, dt$ describes the part of energy transfer that can be linked to changing the position of the piston's center of mass, a macroscopic property. The average force $\langle F_{\text{E}\to\text{P}} \rangle$ can account for the action of a cat on the piston, or even the action of an external gas (see Fig. 7.2).

Furthermore, we note that since the Schrödinger version of the internal energy operator for the gas+piston system $E^{\text{s}}_{\text{S}} = H^{\text{s}}_{\text{G}} + H^{\text{s}}_{\text{P}} + V^{\text{s}}_{\text{PG}}$ is composed only of observables that act in the state space of the system of interest $\mathbb{H}_{\text{G}} \otimes \mathbb{H}_{\text{P}}$, then the Corollary 7.1 can be used, so that $d\langle E_{\text{S}} \rangle - \delta W_{\text{u}} = \text{Tr}[\partial_t \rho_{\text{S}}(t) (E^{\mathfrak{E}}_{\text{S}})^{\text{s}}] dt$, with a format similar to the HB definition of heat. It is interesting to note that the difference $d\langle E_{\text{S}} \rangle - \delta W_{\text{u}}$ is associated with microscopic properties variations of the piston and the gas, which, in general, have a high fluctuation.

Let us now consider the following hypotheses, mimicking macroscopic systems in quasi-equilibrium processes:

- The center of mass moves with practically constant velocity $\langle \dot{X}_{\text{cm}} \rangle$, such that $\langle \ddot{X}_{\text{cm}} \rangle \approx 0$;
- The average force exerted by the gas on the piston,

$$F_{\text{G}\to\text{P}} = \sum_{i \in \text{G}, k \in \text{P}} \left\langle -\partial_{X_k} V_{ik} \left(X_i - (X'_k + X_{\text{cm}}) \right) \right\rangle , \tag{7.55}$$

  equals $p_{\text{isos}} A$, where p_{isos} is the isostatic pressure of the gas and A is the area of the piston.

If these hypotheses are satisfied, then it follows that $\langle \ddot{X}_{\text{cm}} \rangle = F_{\text{G}\to\text{P}} + F_{\text{E}\to\text{P}} \approx 0$, resulting in $F_{\text{E}\to\text{P}} \approx -F_{\text{G}\to\text{P}} = -p_{\text{isos}} A$. Therefore,

$$\delta \mathcal{W}_{\text{u}} \approx -p_{\text{isos}} A \langle \dot{X}_{\text{CM}} \rangle dt. \tag{7.56}$$

[3] Note that the hypotheses (H1) are met in the format (7.49). If the potentials do not diverge, we expect that (H2) is also satisfied.

Since the volume V of the confined gas G satisfies $\dot{V} = A\langle \dot{X}_{\rm cm} \rangle$, we have that

$$\delta \mathcal{W}_{\rm u} \approx -p_{\rm isos} dV \tag{7.57}$$

which is a form usually associated with work in thermodynamics.

Notably, in order for us to ensure that the UQM work can be seen as $-pdV$, the hypotheses we assume would have to be proved, which we did not do here. However, it is interesting to note that, if the system dynamics is such that some assumptions that encapsulate the usual macroscopic behaviors of thermodynamic systems are satisfied, we can obtain usual forms of thermodynamics work in a quantum-mechanical substrate from the UQM work.

7.5 Take-away messages

In the present chapter, we have presented a definition of work that captures the usefulness, trackable nature of the thermodynamics work in both autonomous and non-autonomous scenarios. It can be seen as a part of the energy transfer (and therefore QM work) related to variables of low fluctuation. Summarizing, the following goals were achieved in this chapter:

- We showed, through an example of three particles, how the UQM work can be defined for cases in which a control is imposed or not on a certain property of the system of interest;
- We extended the UQM work to more general scenarios in Section 7.3, where we also showed that UQM work leads to the emergence of the HB notions of work;
- We then showed, for a scenario commonly treated in thermodynamics, that UQM work may lead to a usual form of thermodynamics work, given some restrictions on the observables of the system.

We expect that UQM work can be used for cases of practical relevance. For instance, quantum many-body systems have demonstrated to be an interesting platform for the investigation of collective macroscopic behaviors linked to microscopic quantum resources for autonomous dynamics [152, 153]. In this direction, we aim at investigating whether a form of UQM work can emerge from collective effects possibly related to quantum information resources.

Another interesting arena could be the trapped ion platform [149, 150], which, allowing for a high-level control over the system, might be suitable to the design of study cases of low-dispersion observables which might be linked with UQM work. In fact, the notion of a trackable work being connected with a low-fluctuation quantity and heat with a high fluctuation is implicitly considered in [149].

8 Concluding remarks

We began this thesis highlighting the important role that the concept of work plays in science. Indeed, as we showed throughout this manuscript, work is either directly or indirectly linked with questions of far-reaching importance in physics. Among them, we can enunciate the following ones:

- How do we describe the internal energy of a given system of interest?
- How do we raise the statistics of a two-time physical quantity in a quantum scenario?
- Is energy conserved in quantum mechanics?
- How do measurements energetically disturb a given system?
- Are the stochastic thermodynamics fluctuation theorems valid in any microscopic scenario?
- Is it possible to extract useful work in an autonomous microscopic scenario? How does a notion of thermodynamics work emerge in this context?

Beginning with a definition of quantum mechanical (QM) work, with a well-defined classical limit, we proposed answers for all these questions, assuming genuinely quantum mechanical contexts involving conservative autonomous systems with possibly few particles and strong interactions. As we showed, once we conceive work as a two-time Heisenberg quantum observable, then we learn how to derive the corresponding statistics, without in any way resorting to non-quantum methods. As a consequence, we demonstrated that the work done on a system (i) allows the natural emergence of the concept of internal energy, (ii) has a well-defined spectrum (eventually quantized), (iii) can be prepared as an element of reality via specific measurements, (iv) has an intrinsic quantum fluctuation, and (v) satisfies an uncertainty relation with energy.

We showed that not just work but also other physical quantities such as linear and angular displacement and energy changes can be taken as two-time observables in quantum physics. In this direction, we discussed how the law of conservation of energy can be satisfied in a quantum context and demonstrated how it naturally emerges as an EPR element of reality. Moreover, we computed the energetic disturbance of a given system resulting from measurements on it. In fact, we derived some bounds for such disturbances in terms of BA's measure of irreality.

From the moment we assumed work to be an observable, we deduced some interesting results directly obtained from quantum mechanics formalism. In particular, we were able to deduce many bounds involving the work done on a given system, eventually establishing important connections with information theory.

From a viewpoint closer to thermodynamics, we showed how the state of the working agent can significantly alter fluctuation theorems. In particular, we showed the important role of (classical and quantum) correlations in this context.

Finally, we proposed a trackable-like work (UQM work) connected with observables with small fluctuations whose form significantly goes back to the physical-statistical work. We demonstrated that this definition can be used for either autonomous or non-autonomous (unitarily evolved) systems and converges to usual definitions of quantum thermodynamics at specific limits.

We hope that this thesis can be considered for future research, given the testable results and preliminary ideas presented. In particular, we envisaged throughout this manuscript possible ideas connecting our results with quantum measurements (Chapter 4), Thermodynamics Uncertainty Relations (TURs) (Section 5.4), general bounds on work (Section 5.5), informational resources (Sections 3.2.2 and 5.6), and applications on quantum many-body systems and trapped ions (Chapters 6 and 7).

The results of Chapter 3 and part of Chapter 4 were published in *Physical Review A* [121].

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A Some mathematical formalities

Can work operator be taken as an observable in a formal mathematical sense? Here we propose an answer to this question. Our strategy is to first prove that work is in fact a self-adjoint operator, a very important step to prove other results. Then, we considered the results in the literature to prove that in fact we can construct a spectral representation of operator $W_{\mathrm{E}\to\mathrm{S}}(t_2,t_1)$, so that work can be taken as observable.

A.1 Is work operator self-adjoint?

We notice that since $H_{\mathrm{S}}(t_1)$ and $H_{\mathrm{S}}(t_2)$ are linear operators, then $W_{\mathrm{E}\to\mathrm{S}}(t_2,t_1)$, being a linear combination of both, will also be. If the operators $H_{\mathrm{S}}(t_2)$ and $H_{\mathrm{S}}(t_1)$ are bounded, then we can simply prove that $W_{\mathrm{E}\to\mathrm{S}}(t_2,t_1)$ is self-adjoint from the equality $W^{\dagger}_{\mathrm{E}\to\mathrm{S}}(t_2,t_1) = H^{\dagger}_{\mathrm{S}}(t_2) - H^{\dagger}_{\mathrm{S}}(t_1) = H_{\mathrm{S}}(t_2) - H_{\mathrm{S}}(t_1) = W_{\mathrm{E}\to\mathrm{S}}(t_2,t_1)$. If the operator is unbounded, there may be important subtleties when defining a self-adjoint operator. We first review the definition of adjoint operators for general unbounded, linear operators:

Definition A.1. *(Definition 10.1-2 of [132]): Let*[1] *$T : D(T) \to H$ be a (possibly unbounded) densely defined linear operator in a complex Hilbert space H. Then the Hilbert-adjoint operator $T^{\dagger} : D(T^{\dagger}) \to$ of T is defined as follows. The domain $D(T^{\dagger})$ of $T^{\dagger}$ consists of all $y \in H$ such that there is a $y^* \in H$ satisfying*[2]

$$(Tx, y) = (x, y^*) \tag{A.1}$$

for all $x \in D(T)$. For each such $y \in D(T^{\dagger})$ the Hilbert-adjoint operator $T^{\dagger}$ is then defined in terms of that y^* by

$$y^* = T^{\dagger} y. \tag{A.2}$$

"Densely defined", considered in Definition A.1, is formalized as follows:

Definition A.2. *(Densely defined, page 527 of [132]) T is densely defined in $\mathbb{H}$ if its domain $D(T)$ is dense in $\mathbb{H}$.*

With these definitions in mind, we can thus formally describe a self-adjoint as follows:

Definition A.3. *Let $T : D(T) \to H$ be a linear operator which is densely defined in a complex Hilbert space $\mathbb{H}$. Then T is called a self-adjoint linear operator if*

$$T = T^{\dagger}. \tag{A.3}$$

[1] $D(T)$ here denotes the domain of T.

[2] (a, b) denotes in this chapter the inner product of a and b.

Notice that, because $T = T^\dagger$, then $D(T^\dagger) = D(T)$. With this property and the above definitions in mind, we assume that the energy operators $H_S(t_1)$ and $H_S(t_2)$ are self-adjoint, a very natural assumption for observables in quantum mechanics [132]. Now, they naturally share the same domain, so that we define $\mathfrak{D} := D(H_S(t_1)) = D(H_S(t_2))$. Since they are self-adjoint, we also have that $D(H_S(t_1)) = D(H_S(t_2)) = D(H_S^\dagger(t_1)) = D(H_S^\dagger(t_2))$. So that, for all $x, y \in \mathfrak{D}$, there will be y', y'' in the same space such that

$$(W_{E\to S}(t_2,t_1)x, y) = (H_S(t_2)x, y) - (H_S(t_1)x, y) = (x, y') - (x, y'') \tag{A.4}$$

such that $y' = H_S^\dagger(t_2)y$ and $y'' = H_S^\dagger(t_1)y$. Since the inner product is bilinear, we have that for any $y \in \mathfrak{D}$, there is a $y^* = y' - y''$ such that

$$(W_{E\to S}(t_2,t_1)x, y) = (x, y^*). \tag{A.5}$$

From the definition of adjoint operator, it follows that for every $y \in \mathfrak{D}$, there exist $y^* = W_{E\to S}^\dagger(t_2,t_1)y = (H_S^\dagger(t_2) - H_S^\dagger(t_1))y = (H_S(t_2) - H_S(t_1))y = W_{E\to S}(t_2,t_1)y$. Since $W_{E\to S}(t_2,t_1)$ and $W_{E\to S}^\dagger(t_2,t_1)$ share the same domain $\mathfrak{D}$, we have that $W_{E\to S}^\dagger(t_2,t_1) = W_{E\to S}(t_2,t_1)$ and therefore $W_{E\to S}(t_2,t_1)$ is self-adjoint.

A.1.1 Spectral Theorem

With these definitions in mind, we have the following result:

Theorem A.1. *(Theorem 10.4-2 of [132] or Proposition 9.18 of [154]) The spectrum $\sigma(T)$ of a self-adjoint linear operator $T : D(T) \to H$ is real and closed; here, H is a complex Hilbert space and $D(T)$ is dense in H.*

Since, in principle, the operators in quantum mechanics maps the vectors of a given Hilbert space $\mathbb{H}$ on the same Hilbert space, we have that the above theorem is valid for $H_S(t_2)$ and $H_S(t_1)$ (since $\mathbb{H}$ is dense in itself), and, as well, will be applied for $W_{E\to S}(t_2,t_1)$. Therefore, the spectrum of $W_{E\to S}(t_2,t_1)$, being a self-adjoint linear operator will be real and closed.

This however, gives us no information about the eigenvectors of $W_{E\to S}(t_2,t_1)$. We know that, if $H_S(t_2)$ and $H_S(t_1)$ are compact, then $W_{E\to S}(t_2,t_1)$ as a finite linear combination of both will also be compact. In this case, we have the following Theorem:

Theorem A.2. *(Theorem 7.5.2, [131]) A non-zero compact self-adjoint operator A in a Hilbert space $\mathbb{H}$ has a finite or infinite sequence of orthonormal eigenvectors $\{v_i\}$ corresponding to non-zero eigenvalues $\{\lambda_i\}_i$ which is complete in the range $R(A)$ of the operator A, i.e. for every $f = Ah$, with $h \in H$, the Parseval equality holds:*

$$\|f\|^2 = \sum_i |(v_i, Ah)|^2 = \sum_i |(v_i, f)|^2. \tag{A.6}$$

By complete in the range $R(A)$, we mean:

Definition A.4. *(Definition 4.5.2, [131]) Let X be a normed linear space. A countable system $g_1, g_2 \cdots, \in X$ is said to be complete in X if for any $x \in X$ and any $\epsilon > 0$, there is a finite linear combination of the g_k such that*

$$\left\| x - \sum \alpha_k g_k \right\| \leq \epsilon. \tag{A.7}$$

Now, quantum mechanics has several non-compact operators, as for instance the position, momentum and, in several cases, the Hamiltonian operators. In these cases, we may still obtain similar values as the ones presented before, however, we assume here only that $W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1)$ is a adjoint linear operator (not necessarily bounded):

Theorem A.3. *(Theorem 13.30 of [155]) To every self-adjoint operator A in $\mathbb{H}$ corresponds a unique resolution E of the identity, on the Borel subsets of the real line, such that*

$$(Ax, y) = \int_{-\infty}^{\infty} t dE_{x,y}(t) \quad x \in D(A), y \in H. \tag{A.8}$$

Moreover, E is concentrated on $\sigma(A) \subset (-\infty, \infty)$ (spectrum of A), in the sense that $E(\sigma(A)) = \mathbb{1}$. E will be called the spectral decomposition of A.

To understand this theorem, several definitions must be maid precise:

Definition A.5. *(Definition 12.17 of [155]) Let $\mathfrak{M}$ be a σ-algebra in a set Ω, and let $\mathbb{H}$ be a Hilbert space. In this setting, a resolution of the identity (on $\mathfrak{M}$) is a mapping*

$$E : \mathfrak{M} \to \mathfrak{B}(H) \tag{A.9}$$

with the following properties:

1. *$E(\emptyset) = 0$ and $E(\Omega) = \mathbb{1}$;*
2. *Each $E(\omega)$ is a self-adjoint projection;*
3. *$E(\omega' \cap \omega'') = E(\omega')E(\omega'')$;*
4. *If $\omega' \cap \omega'' = \emptyset$, then $E(\omega' \cup \omega'') = E(\omega') + E(\omega'')$;*
5. *For every $x, y \in H$, the set function $E_{x,y}$ defined by*

$$E_{x,y}(\omega) = (E(\omega)x, y) \tag{A.10}$$

is a complex measure on $\mathcal{M}$.

Definition A.6. *(σ-**algebra**, Definition 1.3, [156]) A collection $\mathfrak{M}$ of subsets of a set X is said to be a σ-algebra in X if $\mathfrak{M}$ has the following three properties:*

1. $X \in \mathfrak{M}$;
2. If $A \in \mathfrak{M}$, then $A^c \in \mathfrak{M}$, where A^c is the complement of A relative to X;
3. If $A = \cup_{n=1}^{\infty} A_n$ and if $A_n \in \mathfrak{M}$ for $n = 1, 2, 3, \cdots$, then $A \in \mathfrak{M}$.

Definition A.7. *(**Borel sets**, [156]) Let X be a topological space. There exists a smallest σ-algebra ($\mathfrak{B}$ in X such that every open set in X belongs to $\mathfrak{B}$. The members of $\mathfrak{B}$ are called the Borel sets of X.*

Definition A.8. *A collection τ of subsets of a set X is said to be a topology in X if τ has the following three properties:*

1. $\emptyset \in \tau$ and $X \in \tau$;
2. If $V_i \in \tau$ for $i = 1, ..., n$, then $V_1 \cap V_2 \cap ... \cap V_n \in \tau$;
3. If $\{V_\alpha\}$ is an arbitrary collection of members of t (finite, countable, or uncountable), then $\cup_\alpha V_\alpha \in \tau$.

If τ is a topology in X, then X is called a topological space, and the members of t are called the open sets in X.

Taking into account definitions A.5-A.8, Theorem A.3 assures us that there will be some self-adjoint projections, $E(\omega)$, that ensures us that $W_{\mathrm{E}\to\mathrm{S}}(t_2, t_1) = \int_{-\infty}^{\infty} t dE(t)$, with the eigenvalues t. It is natural to assume that $E(t)$ can be taken as a projection operator with respect to the eigenvalues t in this operator. However, the theorem does not explicit assume that the t's that appear in the integral are actually the ones that composes the spectrum of A, so that they are not, necessarily, the eigenvalues of A. However, there is another theorem, for a more specific case,

Theorem A.4. *(Theorem 13.33, [155]) Every normal operator N in $\mathbb{H}$ has a unique spectral decomposition E, which satisfies*

$$(Nx, y) = \int_{\sigma(N)} \lambda dE_{x,y}(\lambda) \quad x \in D(N), y \in H. \tag{A.11}$$

A normal operator is defined as:

Definition A.9. *(Definition 13.29, [155]) A (not necessarily bounded) linear operator T in $\mathbb{H}$ is said to be normal if T is closed and densely defined and if $TT^\dagger = T^\dagger T$.*

Aiming completeness, we also define the projection operator as:

Definition A.10. *(Definition 12.11, [155]) An operator $T \in \mathfrak{B}(H)$ is said to be a projection if $T^2 = T$.*

As shown in Theorem 10.3-3 of [132], the adjoint of an operator is closed. Therefore, a self-adjoint operator must be closed. Consequently, work operator, being a self-adjoint operator, is also closed. Being the operators $H_{\mathrm{S}}(t_2)$ and $H_{\mathrm{S}}(t_1)$ densely defined on a Hilbert space $\mathbb{H}$ with the same domain $D(H_{\mathrm{S}}(t_1)) = D(H_{\mathrm{S}}(t_2))$, then work, that will have the same domain, will also be densely defined on $\mathbb{H}$. Therefore, from definition A.9 and the fact that work is self-adjoint, we can assert that the work operator is normal[3] ($W_{\mathrm{E}\to\mathrm{S}}(t_2,t_1) = W^{\dagger}_{\mathrm{E}\to\mathrm{S}}(t_2,t_1) \implies W_{\mathrm{E}\to\mathrm{S}}(t_2,t_1)W^{\dagger}_{\mathrm{E}\to\mathrm{S}}(t_2,t_1) = W^{\dagger}_{\mathrm{E}\to\mathrm{S}}(t_2,t_1)W_{\mathrm{E}\to\mathrm{S}}(t_2,t_1)$). As a result, we can assure ourselves that $W_{\mathrm{E}\to\mathrm{S}}(t_2,t_1)$ has a unique spectral decomposition such that $W_{\mathrm{E}\to\mathrm{S}}(t_2,t_1) = \int_{\sigma(\mathrm{W})} \lambda dE(\lambda)$, where λ are eigenvalues of $W_{\mathrm{E}\to\mathrm{S}}(t_2,t_1)$ and $E(\lambda)$ are projections related to that eigenvalue. Consequently, in the same way as momentum and position operators have a spectral decomposition with corresponding eigenvalues, so as to mathematically characterize them as observables, work operator can also be accounted as such.

[3] This is in fact connected with the mathematical definition of observable proposed by Kreyszig, in page 575 of [132].

B Minimum of an important functional of Chapter 5

We prove in the present Appendix an important relation used to bound work in several manners in Chapter 5. We begin by deducing the more general form of the relation and then we show how it can be regarded for both a constrained and unconstrained cases.

B.1 The deduction itself, bipartide state

Consider a Hilbert space $\mathbb{H}$, on which an operator A acts. This space can be bipartide ($\mathbb{H} = \mathbb{H}_{\mathrm{S}} \otimes \mathbb{H}_{\mathrm{E}}$) or not. Our task in this Section is to deduce the following result:

Theorem B.1. *Given the definition of the von Neumann entropy* $S(\rho) = -\operatorname{Tr}[\rho \ln \rho]$ *and real positive constants* ν *and* $T_\nu = (\nu)^{-1}$*, the state*

$$\rho_\nu^A := \frac{\mathrm{e}^{-\nu A}}{\mathcal{Z}_A^\nu}, \quad \mathcal{Z}_A^\nu = \operatorname{Tr}\left[\mathrm{e}^{-\nu A}\right] \tag{B.1}$$

minimizes the functional

$$F_A = \langle A \rangle - T_\nu S(\rho) = \operatorname{Tr} \rho A + T_\nu \operatorname{Tr} \rho \ln \rho. \tag{B.2}$$

Proof. Let us first consider the map Φ, described in Chapter 4 as[1]

$$\Phi_A(\rho) = \sum_k |a_k\rangle \langle a_k| \rho |a_k\rangle \langle a_k| = \sum_k |a_k\rangle \langle a_k| p_k \tag{B.3}$$

where $p_k = \operatorname{Tr}[|a_k\rangle \langle a_k| \rho]$ and $|a_k\rangle \langle a_k|$ are projectors related to $A = \sum_k a_k |a_k\rangle \langle a_k|$. As a result, we have that

$$\operatorname{Tr}[\Phi_A(\rho) A] = \operatorname{Tr}[\rho A] \tag{B.4}$$

Also, it follows that [111]

$$S(\Phi_A(\rho)) = -\operatorname{Tr}[\rho \ln \Phi_A(\rho)] = -\sum_i p_i \ln p_i \geq -k \operatorname{Tr} \rho \ln \rho. \tag{B.5}$$

Regarding both relations (B.4) and (B.5), we deduce that

$$F_A(\rho) - F_A(\Phi_A(\rho)) = T_\nu (S(\Phi_A(\rho)) - S(\rho)) \geq 0, \tag{B.6}$$

for $T_\nu \geq 0$. Consequently, for any given state ρ, its decohered version $\Phi_A(\rho)$ will always have a smaller or equal F_A. It means that the state that minimizes F_A must have the form

[1] Here we have considered a discrete basis, but it can be extended for continuum basis, as shown in [118]. Moreover, we consider that the eigenvectors $|a_k\rangle$ are defined for the whole Hilbert space. If $A = A_{\mathrm{L}} \otimes \mathbb{1}_{\mathrm{E}}$, i.e. if A can be written in terms of a local operator A_{L} times the identity on the space $\mathbb{H}_{\mathrm{E}}$ then, after few adaptations, it can be proved that the result of the theorem is obtained as well.

$\rho = \Phi_A(\rho)$. Now, to prove the result, we need to compute the minimum possible value of $F(\Phi_A(\rho))$. To do so, we minimize it with respect to p_k, taking into account a Lagrangean multiplier γ to restrict the state so that $\mathrm{Tr}(\Phi_A(\rho)) = \sum_k p_k = 1$ [103], so that

$$\delta F_A(\Phi_A(\rho)) + \gamma\delta \,\mathrm{Tr}\, \Phi_A(\rho) = \delta \langle A\rangle - T_\nu \delta S(\Phi_A(\rho)) + \gamma\delta \,\mathrm{Tr}\, \Phi_A(\rho) = 0 \tag{B.7}$$

where δ in the present Appendix refers to the usual small variations/perturbations of minimization problems[2]. Considering

$$\begin{aligned} \delta \langle A\rangle &= \delta \,\mathrm{Tr}\,[\Phi_A(\rho)A] = \textstyle\sum_i (\delta p_i) a_i, \\ \delta S(\Phi_A(\rho)) &= -\textstyle\sum_i \delta p_i \ln p_i - \sum_i p_i \frac{\delta p_i}{p_i} = -\sum_i \delta p_i (\ln p_i + 1), \\ \delta \,\mathrm{Tr}\, \Phi_A(\rho) &= \delta \textstyle\sum_i p_i = \sum_i \delta p_i, \end{aligned} \tag{B.8}$$

we deduce

$$\delta F(\Phi_A(\rho)) + \gamma \,\mathrm{Tr}\, \Phi_A(\rho) = \sum_i \delta p_i (a_i + T_\nu(\ln p_i + 1) + \gamma) = 0 \tag{B.9}$$

So that for the minimum to occur, it is sufficient that:

$$a_i + T_\nu(\ln p_i + 1) + \gamma = 0 \tag{B.10}$$

so that, with $\nu = T_\nu^{-1}$

$$p_i = \exp[-\nu(a_i + \gamma) - 1] \tag{B.11}$$

Now, since $\sum_i p_i = 1$, we have that

$$1 = \sum_i p_i = \sum_i \exp[-\nu(a_i + \gamma) - 1] = \exp[-\nu\gamma - 1] \sum_i \exp[-\nu(a_i)] \tag{B.12}$$

which implies

$$\exp[-\nu\gamma - 1] = \frac{1}{\sum_i \exp[-\nu(a_i)]} = \frac{1}{\mathcal{Z}_A^\nu} \tag{B.13}$$

where $\mathcal{Z}_A^\nu = \sum_i \exp[-\nu(a_i)] = \mathrm{Tr}[\mathrm{e}^{-\nu A}]$ so that,

$$p_i = \frac{\exp[-\nu(a_i)]}{\mathcal{Z}_A}. \tag{B.14}$$

Therefore, among all the states ρ, the state that minimizes $F_A(\Phi_A(\rho))$, and therefore of $F_A(\rho)$, is

$$\rho_\nu^A := \frac{\mathrm{e}^{-\nu A}}{\mathcal{Z}_A^\nu}, \quad \mathcal{Z}_A^\nu = \mathrm{Tr}\left[\mathrm{e}^{-\nu A}\right] \tag{B.15}$$

so that

$$F(\rho_\nu^A) = \min_\rho F(\rho). \tag{B.16}$$

□

[2] In fact, δ may be substituted by the gradient with respect to the probabilities p_k, as the computations in Section B.2 show.

It is important to highlight here that A may acts on a bipartide Hilbert space $\mathbb{H} = \mathbb{H}_S \otimes \mathbb{H}_E$, and A can be equal to an operator $A \otimes \mathbb{1}_E$; the above theorem should still be valid.

Also, notice that

$$TS(\rho_\nu^A) = -T_\nu \operatorname{Tr}\left[\frac{\exp[-\nu(a_i)]}{\mathcal{Z}_A^\nu}.(-\nu a_i - \ln \mathcal{Z}_A^\nu)\right] = \langle A \rangle_{\rho_A^\nu} + T_\nu \ln \mathcal{Z}_A^\nu \tag{B.17}$$

so that

$$F_A(\rho) \geq F_A(\rho_\nu^A) = -T_\nu \ln \mathcal{Z}_A^\nu. \tag{B.18}$$

B.2 Mathematical point of view: is it a minimum or maximum?

We show now, how the minimization problem solved in Theorem B.1 can be seen either as a constrained ($\langle A \rangle = X$, where X is a predefined real value) or unconstrained problem and that the solution ρ_ν^A indeed minimizes (and is not a saddle point or maximize) F_A.

B.2.1 Constrained problem

Consider the following problem:

$$\begin{aligned} \min_x \quad & f(x) \\ \text{such that} \quad & c_I(x) \leq 0 \\ & c_E(x) = 0 \end{aligned} \tag{B.19}$$

where $x \in \mathbb{R}^n$, $f : \mathbb{R}^n \to \mathbb{R}$ $c_i : \mathbb{R}^n \to \mathbb{R}$, for $i \in \{I, E\}$ and both functions are 2-time differentiable. This is a problem where we can impose both type of restrictions (E and I): a function which the system must satisfy ($c_E(x) = 0$) and another that the system cannot surpass ($c_I(x) \leq 0$). For instance, if $n = 2$ and $x = (x_1, x_2)$, then $c_E(x) = x_1^2 - x_2^2 - 4$ and $c_i(x) = -x_1^2 + 1$ implies that the solution should be such that $1 \leq x_1 = \pm\sqrt{x_2^2 - 4}$.

Now, the Karush-Kuhn-Tucker (KKT) theorem is stated as follows:

Theorem B.2. *(KKT, Theorem 7.25 of [157]) Let $\mathbf{x}^* \in \Omega \subset \mathbb{R}^n$ be a local minimum of the problem B.19 and suppose that $P(T(\mathbf{x}^*)) = P(D(\mathbf{x}^*))$[3]. Then there exists vectors $\boldsymbol{\lambda}^*$ and $\boldsymbol{\mu}^*$ such that*

$$\nabla f(\mathbf{x}^*) + \sum_{j \in E} \lambda_j^* \nabla c_j(\mathbf{x}^*) + \sum_{i \in I} \mu_i^* \nabla c_i(\mathbf{x}^*) = 0 \tag{B.20}$$

where for every $i \in I$,

$$\mu_i^* \geq 0 \tag{B.21}$$

and

$$\mu_i^* c_I(\mathbf{x}^*) = 0. \tag{B.22}$$

[3] $P(S)$ is the polar set with respect to the set S and $T(\mathbf{x}^*)$ and $D(\mathbf{x}^*)$ are respectively the tangent and linearized feasible cone. This condition can be restated as I will soon address.

Now, for our case, we only considered one equality restriction, so that the version that we considered is

$$\nabla f(\mathbf{x}^*) + \nu \nabla c_1(\mathbf{x}^*) + \gamma c_2(\mathbf{x}^*) = 0 \tag{B.23}$$

which, substituting $\mathbf{x} \to \mathbf{p} \equiv (p_1, p_2, ...)$, $f(\mathbf{p}) = \sum_i p_i \ln p_i$, $c_1(\mathbf{p}) = \sum_i p_i a_i - X$ and $c_2(\mathbf{p}) = \sum_i p_i - 1$ in Eq. (B.20), gives us exactly (B.10). Notice that we consider $f(\mathbf{p}) = -S(\Phi_A(\rho))$, i.e. minus the entropy, since we want to maximize it.

Now, we must see if condition $P(T(\mathbf{x}^*)) = P(D(\mathbf{x}^*))$ is satisfied. In this direction, there is a Theorem that helps us:

Theorem B.3. *A feasible point $\mathbf{x}^*$ (that is, that satisfies the restrictions) satisfies the conditions from KKT theorem iff*

$$0 = d^c(\mathbf{x}^*) = Proj_{\mathcal{L}(\mathbf{x}^*)}(\mathbf{x}^* - \nabla f(\mathbf{x}^*)) - \mathbf{x}^* \tag{B.24}$$

where

$$Proj_{\mathcal{L}(\mathbf{x}^*)}(y) = \min_{\mathbf{z} \in \mathcal{L}(\mathbf{x}^*)} \|\mathbf{z} - \mathbf{y}\| \tag{B.25}$$

and

$$\mathcal{L}(\mathbf{x}^*) = \{\mathbf{x}^* + \mathbf{d} \in \mathbb{R}^n | c_E(\mathbf{x}^*) + \nabla c_E(\mathbf{x}^*)^T \mathbf{d} = 0, c_E(\mathbf{x}^*) + \nabla c_I(\mathbf{x}^*)^T \mathbf{d} \leq 0\} \tag{B.26}$$

Therefore, we have to find out whether $\mathbf{x}^*$ satisfies

$$\mathbf{x}^* = \text{Proj}_{\mathcal{L}(\mathbf{x}^*)}(\mathbf{x}^* - \nabla f(\mathbf{x}^*)) \tag{B.27}$$

This is the same as find out whether $\mathbf{d} = 0$ is the one that minimizes

$$\|\mathbf{x}^* + \mathbf{d} - \mathbf{x}^* + \nabla f(\mathbf{x}^*)\| = \|\mathbf{d} + \nabla f(\mathbf{x}^*)\| \tag{B.28}$$

such that $\mathbf{d}$ satisfies

$$c_E(\mathbf{x}^*) + \nabla c_E(\mathbf{x}^*)^T \mathbf{d} = 0, c_E(\mathbf{x}^*) + \nabla c_I(\mathbf{x}^*)^T \mathbf{d} \leq 0 \tag{B.29}$$

Now, since $\mathbf{d}$ satisfies (B.29), and, in our case

$$\nabla f(\mathbf{x}^*) = -\sum_{j \in E} \lambda_j^* \nabla c_j(\mathbf{x}^*), \tag{B.30}$$

then

$$\nabla f(\mathbf{x}^*)^T d = -\sum_{j \in E} \lambda_j^* \nabla c_j(\mathbf{x}^*)^T \mathbf{d} = 0, \tag{B.31}$$

so that

$$\|\mathbf{d} + \nabla f(\mathbf{x}^*)\| = \|\mathbf{d}\| + \|\nabla f(\mathbf{x}^*)\| \tag{B.32}$$

which is minimum for $\mathbf{d} = 0$, so that $0 = d^c(\mathbf{x}^*) = \text{Proj}_{\mathcal{L}(\mathbf{x}^*)}(\mathbf{x}^* - \nabla f(\mathbf{x}^*)) - \mathbf{x}^*$, and as a consequence of the theorem, our solution is a local minimum. Since the correspondent state is the unique that satisfy the KKT theorem, then it is the global minimum.

B.2.2 Unconstrained case

Theorem B.4. *(Second order sufficient condition) Let $f : \mathbb{R}^n \to \mathbb{R}$ two-time differentiable at $\mathbf{x}^* \in \mathbb{R}^n$. If $\mathbf{x}^*$ is a stationary point of f ($\boldsymbol{\nabla} f(\mathbf{x}^*) = 0$), and the Hessian matrix of f in $\mathbf{x}^*$ is positive definite, then $\mathbf{x}^*$ is a local minimum.*

Therefore, all we need to check is whether for any non-null $\mathbf{d} \in \mathbb{R}^n$

$$\mathbf{d}^T(\boldsymbol{\nabla}^2 f)\mathbf{d} > 0. \tag{B.33}$$

Now, we have from (B.10), that

$$(\boldsymbol{\nabla} f)_i = \partial_{p_i} f = a_i + T_\nu(\ln p_i + 1) + \gamma \tag{B.34}$$

The Hessian is therefore

$$(\boldsymbol{\nabla} f)_{ij} = \partial_{p_j}(a_i + T_\nu(\ln p_i + 1) + \gamma) = T_\nu \frac{\delta_{ij}}{p_i} \tag{B.35}$$

So that

$$\mathbf{d}^T(\boldsymbol{\nabla}^2 f)\mathbf{d} = \sum_{ij} d_i T_\nu \frac{\delta_{ij}}{p_i} d_j = \sum_i d_i T_\nu \frac{1}{p_i} d_i > 0. \tag{B.36}$$

So it is in the unconstrained case, it is a minimum also.

C Results of Chapter 6

We aim here at expressing for the many different (quantum) scenarios considered throughout the main text in Chapter 6 (i) that particle 1 reduced state is sufficiently close to a thermal state and (ii) the expressions for $\langle e^{-\beta W}\rangle$. We consider each scenario individually.

C.1 Thermal-Gaussian (TG) and thermal-thermal (TT) states

In the very first scenario, we considered the following state for the whole system:

$$\rho_{\text{TG}} = T_{\Delta_1}(\sigma_1) \otimes G_{\bar{\mathbf{r}}_2,\sigma_2}, \tag{C.1}$$

where $G_{\bar{\mathbf{r}}_2,\sigma_2} = |\bar{\mathbf{r}}_2\rangle\langle\bar{\mathbf{r}}_2|$ denotes a pure Gaussian state, meaning that

$$\begin{aligned}\langle x_2|\bar{\mathbf{r}}_2\rangle &= \left(\frac{2\sigma_2^2}{\pi\hbar^2}\right)^{1/4} e^{-\frac{\sigma_2^2(x_2-\bar{x}_2)^2}{\hbar^2}+\frac{i\bar{p}_2 x_2}{\hbar}},\\ \langle p_2|\bar{\mathbf{r}}_2\rangle &= \frac{1}{\left(2\pi\sigma_2^2\right)^{1/4}} e^{-\frac{(p_2-\bar{p}_2)^2}{4\sigma_2^2}-\frac{i(p_2-\bar{p}_2)\bar{x}_2}{\hbar}},\end{aligned} \tag{C.2}$$

where $\bar{\mathbf{r}}_2 = (\bar{x}_2, \bar{p}_2)$. For the receiver, we consider the effective thermal state

$$T_{\Delta_1}(\sigma_1) = \int \mathrm{d}p \, \frac{e^{-\frac{p^2}{2\Delta_1^2}}}{\sqrt{2\pi\Delta_1^2}} G_{(0,p),\sigma_1}, \tag{C.3}$$

where we recall that $\Delta_1 = \sqrt{m_1/\beta_1}$. We first show that $T_{\Delta_1}(\sigma_1)$ is actually close to a thermal state. For that, we compute $\langle p_1'|\, T_{\Delta_1}(\sigma_1)\,|p_1\rangle$, so as to analyze its components:

$$\begin{aligned}\langle p_1'|\, T_{\Delta_1}(\sigma_1)\,|p_1\rangle &= \int \mathrm{d}p \, \frac{e^{-\frac{p^2}{2\Delta_1^2}}}{\sqrt{2\pi\Delta_1^2}} \langle p_1'|\, G_{(0,p),\sigma_1}\,|p_1\rangle\\ &= \frac{1}{\sqrt{2\pi(\Delta_1^2+\sigma_1^2)}} \exp\left[-\frac{p_1'^2+p_1^2}{4(\Delta_1^2+\sigma_1^2)} - \frac{\frac{\Delta_1^2}{\sigma_1^2}(p_1'-p_1)^2}{8(\Delta_1^2+\sigma_1^2)}\right].\end{aligned} \tag{C.4}$$

In the limit in which $\frac{\sigma_1}{\Delta_1} \equiv \epsilon \to 0$, i.e. the thermal fluctuations Δ_1, are very high when compared to the Gaussian uncertainties σ_1, it is straightforwardly deduced that

$$\begin{aligned}\langle p_1|\, T_{\Delta_1}(\sigma_1)\,|p_1\rangle &\to \frac{e^{-\frac{p^2}{2\Delta_1^2}}}{\sqrt{2\pi\Delta_1^2}}\\ \langle p_1'|\, T_{\Delta_1}(\sigma_1)\,|p_1\rangle &\to 0, \quad \text{if} \quad p_1' \neq p_1.\end{aligned} \tag{C.5}$$

Therefore, in the limit $\frac{\sigma_1}{\Delta_1} \to 0$, $T_{\Delta_1}(\sigma_1)$ is approximately a state with no coherence terms and diagonalized in the momentum of particle 1 basis, with a thermal distribution $\langle p_1|T_{\Delta_1}(\sigma_1)|p_1\rangle = \mathrm{e}^{-\beta K_1}/\sqrt{2\pi\Delta_1^2}$, in terms of the kinetic energy $K_1 = p_1^2/2m_1$.

For general σ_1 and Δ_1, we consider Eqs.(6.24) and (6.25), here rewritten for convenience,

$$w_{p_1,p_2} = \frac{2}{M^2}(m_1p_2 - m_2p_1)(p_1 + p_2), \tag{C.6}$$

$$\langle f(W)\rangle_\rho = \iint_{-\infty}^{\infty} dp_1dp_2 f(w_{p_1,p_2}) \langle p_1p_2|\,\rho\,|p_1p_2\rangle, \tag{C.7}$$

so as to obtain, after substituting $f(W) = \mathrm{e}^{-\beta_1 W}$, the relation

$$\begin{aligned}\langle \mathrm{e}^{-\beta_1 W}\rangle_{\rho_{\mathrm{TG}}} &= \iint_{-\infty}^{\infty} dp_1dp_2\, \mathrm{e}^{-\beta_1 w_{p_1,p_2}} \langle p_1p_2|\,\rho_{\mathrm{TG}}\,|p_1p_2\rangle \\ &= \frac{(m_1+m_2)\exp\left(\frac{2\beta_1^2\sigma_1^2\bar{p}_2^2}{-4\beta_1^2\sigma_1^2\sigma_2^2+m_1^2-2m_1m_2+m_2^2-4\beta_1\sigma_1^2m_2}\right)}{\sqrt{-4\beta_1^2\sigma_1^2\sigma_2^2 + m_1^2 - 2m_1m_2 + m_2^2 - 4\beta_1\sigma_1^2m_2}}.\end{aligned} \tag{C.8}$$

with the convergence condition that $-4\beta_1^2\sigma_1^2\sigma_2^2 + m_1^2 - 2m_1m_2 + m_2^2 - 4\beta_1\sigma_1^2m_2 > 0$. It is easy to check that when $m_1, m_2 \neq 0$, σ_2 and $\hbar/\sigma_2$ are bounded, and $\frac{\sigma_1}{\Delta_1} = \frac{\sigma_1}{\sqrt{m_1/\beta_1}} \to 0$, (C.8) reduces to

$$\langle \mathrm{e}^{-\beta_1 W}\rangle_{\rho_{\mathrm{TG}}} = \frac{m_1+m_2}{|m_2-m_1|}, \tag{C.9}$$

therefore accounting (6.30) in the main text.

If both $\frac{\sigma_1}{\Delta_1} = \epsilon$ and $\frac{\Delta_1}{\sigma_2} \equiv \frac{\epsilon}{\gamma}$ ($\gamma = \sigma_1\sigma_2/\Delta_1^2$) and $\epsilon \ll 1$, i.e., not only σ_1 is small when compared with Δ_1 but also σ_2 tends to be very high when compared to it, so that $\frac{\hbar}{2\sigma_2} \to 0$, then

$$\langle \mathrm{e}^{-\beta_1 W}\rangle_{\rho_{\mathrm{TG}}} = \frac{m_1+m_2}{|m_2-m_1|}\,\Gamma. \tag{C.10}$$

where $\Gamma \equiv \left[1 - \left(\frac{2m_1\gamma}{m_1-m_2}\right)^2\right]^{-\frac{1}{2}}$.

Regarding a similar procedure as above, but for the state

$$\rho_{\mathrm{TT}} = T_{\Delta_1}(\sigma_1) \otimes T_{\Delta_2}(\sigma_2), \tag{C.11}$$

that is, now particle 2 reduced state is also a thermal-like state $T_{\Delta_2}(\sigma_2)$ of temperature β_2, then it follows

$$\langle \mathrm{e}^{-\beta_1 W}\rangle_{\rho_{\mathrm{TT}}} = \frac{(m_1+m_2)}{\sqrt{-4\beta_1^2\sigma_1^2\sigma_2^2 + m_1^2 - 2m_1m_2 + m_2^2 - 4\frac{\beta_1}{\beta_2}\sigma_1^2m_2(\beta_1+\beta_2)}}, \tag{C.12}$$

with $-4\beta_1^2\sigma_1^2\sigma_2^2 + m_1^2 - 2m_1m_2 + m_2^2 - 4\frac{\beta_1}{\beta_2}\sigma_1^2m_2(\beta_1+\beta_2) > 0$. Regarding the same conditions to deduce (C.9) and (C.10), we obtain the same results

$$\langle \mathrm{e}^{-\beta_1 W}\rangle_{\rho_{\mathrm{TT}}} = \frac{m_1+m_2}{|m_2-m_1|}. \tag{C.13}$$

and

$$\langle \mathrm{e}^{-\beta_1 W}\rangle_{\rho_{\mathrm{TT}}} = \frac{m_1+m_2}{|m_2-m_1|}\,\Gamma. \tag{C.14}$$

C.2 Agent in quantum superposition

We consider now the following preparation for the whole state system is

$$\rho_{\text{TS}} = T_{\Delta_1}(\sigma_1) \otimes \frac{(\xi + \chi)}{N}, \tag{C.15}$$

where

$$\begin{aligned} \xi &= |\bar{\mathbf{r}}_2\rangle \langle \bar{\mathbf{r}}_2| + |\bar{\mathbf{r}}_2'\rangle \langle \bar{\mathbf{r}}_2'|, \\ \chi &= |\bar{\mathbf{r}}_2\rangle \langle \bar{\mathbf{r}}_2'| + |\bar{\mathbf{r}}_2'\rangle \langle \bar{\mathbf{r}}_2|, \end{aligned} \tag{C.16}$$

with $|\bar{\mathbf{r}}_2\rangle$ and $|\bar{\mathbf{r}}_2'\rangle$ Gaussians state with center at $\bar{\mathbf{r}}_2 = (\bar{x}_2, \bar{p}_2)$ and $\bar{\mathbf{r}}_2' = \bar{\mathbf{r}}_2 + (\delta_x, 0)$, respectively, and momentum uncertainty σ_2. δ_x is a generic spatial displacement and the normalization factor is given $N = \text{Tr}\,(\chi + \xi) = 2\big[1 + \exp(-\frac{\delta_x^2\sigma_2^2}{2\hbar^2})\big]$. Regarding ρ_{TS}, we compute the exact expression:

$$\langle \mathrm{e}^{-\beta_1 W} \rangle_{\rho_{\text{TS}}} = \frac{(m_1 + m_2) \exp\left(\frac{2\beta_1^2\sigma_1^2\bar{p}_2^2}{(m_1-m_2)^2 - 4\beta_1^2\sigma_1^2\sigma_2^2 - 4\beta_1\sigma_1^2 m_2}\right) \Omega}{(1 + \exp[-(\delta_x^2\sigma_2^2)/2\hbar^2]) \sqrt{(m_1 - m_2)^2 - 4\beta_1^2\sigma_1^2\sigma_2^2 - 4\beta_1\sigma_1^2 m_2}}, \tag{C.17}$$

where

$$\begin{aligned} \Omega &= 1 + \exp\left(-\Theta\left((m_1 - m_2)^2 - 4\beta_1\sigma_1^2 m_2\right)\right) \cos\left(\frac{8\beta_1^2\sigma_1^2\hbar\bar{p}_2\Theta}{\delta_x}\right), \\ \Theta &= \frac{\sigma_2^2\delta_x^2}{2\hbar^2\left((m_1 - m_2)^2 - 4\beta_1^2\sigma_1^2\sigma_2^2 - 4\beta_1\sigma_1^2 m_2\right)}, \end{aligned} \tag{C.18}$$

with the condition $-4\beta_1^2\sigma_1^2\sigma_2^2 + m_1^2 - 2m_1m_2 + m_2^2 - 4\beta_1\sigma_1^2 m_2 > 0$.

We can analyze several different scenarios with state ρ_{TS}. First, let us consider a case in which the local state of particle 1 is approximately a thermal state, and no restriction is imposed to the initial state of particle 2. In this case, we take $\frac{\sigma_1}{\Delta_1} = \epsilon \to 0$, so as to obtain

$$\langle \mathrm{e}^{-\beta W} \rangle_{\rho_{\text{TS}}} = \frac{m_1 + m_2}{|m_1 - m_2|} \tag{C.19}$$

which does not differ from the Gaussian nor thermal state scenarios. We can, instead, consider the interesting scenario in which both $\frac{\sigma_1}{\Delta_1} = \epsilon$ and $\frac{\Delta_1}{\sigma_2} \equiv \frac{\epsilon}{\gamma}$ with $\epsilon \to 0$ are valid, so that the Gaussian packages of particle 2 has a very sharp distribution in terms of position with momentum $\bar{p}_2$. By also denoting $\eta \equiv 2\sigma_2\delta_x/\hbar$, we consider expression (6.2) to deduce:

$$\langle \mathrm{e}^{-\beta_1 W} \rangle_{\rho_{\text{TS}}} \cong \frac{(m_1 + m_2)}{|m_1 - m_2|} \Gamma\, \Xi, \tag{C.20}$$

where $\Xi \equiv \frac{1+\exp\left(-\eta^2\Gamma^2/8\right)}{1+\exp(-\eta^2/8)}$. In this scenario, we can analyze the role of interference, as done throughout the main text in Chapter 6.

Interestingly, if we additionally consider that $\frac{\bar{p}_2}{\Delta_1} = \frac{\gamma'}{\epsilon}$, with $\epsilon \to 0$, i.e., that the momentum of the particle 2 wave package are extremely high, then a phase-like term appear as well, so that

$$\langle e^{-\beta W} \rangle_{\rho_{\beta S}} = \frac{(m_1 + m_2) \exp\left(\frac{2m_1^2\gamma'^2}{(m_1-m_2)^2-4m_1^2\gamma}\right) \Omega'}{(1 + \exp[-\delta_x^2\sigma_2^2/2\hbar^2]) \sqrt{(m_1 - m_2)^2 - 4m_1^2\gamma^2}}, \tag{C.21}$$

where now

$$\begin{aligned} \Omega' &= 1 + \exp\left(-\Theta\left((m_1 - m_2)^2\right)\right) \cos\left(\frac{8m_1^2\gamma'^2\hbar\Theta'}{\delta_x}\right), \\ \Theta' &= \frac{\eta^2}{8\left((m_1 - m_2)^2 - 4m_1^2\gamma^2\right)}, \end{aligned} \tag{C.22}$$

C.3 Entanglement between particle 1 and 2

We consider now, an entangled initial state $\rho_e = |\psi\rangle\langle\psi|$, where

$$|\psi\rangle = \int dp \frac{e^{-\frac{p^2}{4\Delta_1^2}}}{\sqrt{N}} |0, p\rangle \otimes |ep, 0\rangle, \tag{C.23}$$

$\Delta_1 = \sqrt{m_1/\beta_1}$ again, N is a normalization constant,

$$N = \frac{4\pi}{\sqrt{\frac{\alpha^2\beta m_1\sigma_p'^2 + \beta\sigma_x^2\left(\beta\sigma_p'^2 + m_1\right)}{m_1^2\sigma_p'^2\sigma_x^2}}} \tag{C.24}$$

$|0, p\rangle$ is a receiver's Gaussian state with center at the mean phase space point $\bar{\mathbf{r}}_1 = (0, p)$ and momentum uncertainty σ_1, $|ep, 0\rangle$ is an agent's Gaussian state with center at the mean phase space point $\bar{\mathbf{r}}_2 = (ep, 0)$ and momentum uncertainty σ_2. Whenever nonzero, the parameter e regulates the correlation of the receiver's momentum with the agent's position. In the limits $\sigma_1 \to 0$ and $\sigma_2 \to \infty$, the Gaussian states $|0, p\rangle$ and $|ep, 0\rangle$ approach momentum and position eigenstates, for the respective particles, with $|\psi\rangle$ thus representing a highly entangled state.

The reduced states are

$$\rho_1 = \mathrm{Tr}_2\left(|\psi\rangle\langle\psi|\right) = \frac{1}{N}\iint_{-\infty}^{\infty} dp\, dp' \exp\left[-\frac{\beta_1 p'^2}{4m_1} - \frac{\beta_1 p^2}{4m_1} - \frac{e^2\sigma_2^2(p' - p)^2}{2\hbar^2}\right] |0, p\rangle\langle 0, p'| \tag{C.25}$$

and

$$\rho_2 = \mathrm{Tr}_1\left(|\psi\rangle\langle\psi|\right) = \frac{1}{N}\iint_{-\infty}^{\infty} dp\, dp' \exp\left[-\frac{\beta_1 p'^2}{4m_1} - \frac{\beta_1 p^2}{4m_1} - \frac{(p' - p)^2}{8\sigma_1^2}\right] |ep, 0\rangle\langle ep, 0|, \tag{C.26}$$

where we can check that

$$\langle p_1'|\,\rho_1\,|p_1\rangle = \frac{1}{\sqrt{2\pi\,\Delta_1^2\left(1+\frac{\sigma_1^2}{\Delta_1^2}\right)}}\exp\left[-\frac{\left(p_1^2+p_1'^2\right)}{4\Delta_1^2\left(1+\frac{\sigma_1^2}{\Delta_1^2}\right)}-\frac{\mathrm{e}^2\sigma_2^2(p_1-p_1')^2}{2\hbar^2\left(1+\frac{\sigma_1^2}{\Delta_1^2}\right)\left(1+\frac{\sigma_1^2}{\Delta_1^2}+\frac{4\mathrm{e}^2\sigma_2^2\sigma_1^2}{\hbar^2}\right)}\right] \tag{C.27}$$

and

$$\begin{aligned}\langle x_2'|\,\rho_2\,|x_2\rangle \;&=\frac{1}{\sqrt{2\pi\Delta_1^2\left(\frac{\hbar^2}{4\sigma_2^2\sigma_1^2}\left(\mathrm{e}^2\frac{4\sigma_2^2\sigma_1^2}{\hbar^2}+\frac{\sigma_1^2}{\Delta_1^2}\right)\right)}}\times\\ &\times\exp\left[-\frac{x^2+x'^2}{4\Delta_1^2\left(\frac{\hbar^2}{4\sigma_2^2\sigma_1^2}\left(\mathrm{e}^2\frac{4\sigma_1^2\sigma_2^2}{\hbar^2}+\frac{\sigma_1^2}{\Delta_1^2}\right)\right)}-\frac{2\mathrm{e}^2\sigma_2^4\sigma_1^2(x-x')^2}{\hbar^4\left(\mathrm{e}^2\frac{4\sigma_1^2\sigma_2^2}{\hbar^2}+\frac{\sigma_1^2}{\Delta_1^2}\right)\left(1+\frac{\sigma_1^2}{\Delta_1^2}+\frac{4\mathrm{e}^2\sigma_1^2\sigma_2^2}{\hbar^2}\right)}\right].\end{aligned} \tag{C.28}$$

Therefore, if $\frac{\sigma_1}{\Delta_1}=\epsilon$ and $\frac{\hbar}{2\sigma_2\Delta_\mathrm{e}}=\vartheta_\mathrm{e}\epsilon$, with $\Delta_\mathrm{e}=\mathrm{e}\Delta_1$ and $\vartheta_\mathrm{e}=\hbar/(2\mathrm{e}\sigma_1\sigma_2)$, then when $\epsilon\to 0$, we deduce that

$$\langle p_1|\rho_1|p_1\rangle \cong \sqrt{\frac{\beta_1}{2\pi m_1}}\;\mathrm{e}^{-\frac{\beta_1 p_1^2}{2m_1}}, \tag{C.29}$$

$$\langle p_1'|\rho_1|p_1\rangle \cong 0 \quad \text{if } p_1'\neq p_1,$$

and

$$\langle x_2|\rho_2|x_2\rangle \cong \frac{1}{\sqrt{2\pi\Delta_\mathrm{e}^2}}\;\mathrm{e}^{-\frac{x_2^2}{2\Delta_\mathrm{e}^2}}, \tag{C.30}$$

$$\langle x_2'|\rho_2|x_2\rangle \cong 0 \quad \text{if } x_2'\neq x_2.$$

We now consider the purity of the local states to compute the entanglement measure $E=1-\mathrm{Tr}\left(\rho_1^2\right)=1-\mathrm{Tr}\left(\rho_1^2\right)$, with the following exact form:

$$\begin{aligned}1-\mathrm{Tr}_1(\rho_1^2) \;&=1-\iint_{-\infty}^{\infty}dp_1dp_1'\,\langle p_1|\,\rho_1\,|p_1'\rangle\,\langle p_1'|\,\rho_1\,|p_1\rangle\\ &=1-\sqrt{\frac{\frac{\sigma_1^2}{\Delta_1^2}\left(1+\frac{\sigma_1^2}{\Delta_1^2}+\frac{4\mathrm{e}^2\sigma_1^2\sigma_2^2}{\hbar^2}\right)}{\left(1+\frac{\sigma_1^2}{\Delta_1^2}\right)\left(\frac{\sigma_1^2}{\Delta_1^2}+\frac{4\mathrm{e}^2\sigma_1^2\sigma_2^2}{\hbar^2}\right)}}\\ &=1-\mathrm{Tr}_2(\rho_2^2)\end{aligned} \tag{C.31}$$

Neglecting second order terms of $\frac{\sigma_1}{\Delta_1}\equiv\epsilon$, and taking into account $\vartheta_\mathrm{e}=\hbar/(2\mathrm{e}\sigma_1\sigma_2)$, we deduce

$$E=1-\mathrm{Tr}\,\rho_2^2\cong 1-\epsilon\sqrt{1+\vartheta_\mathrm{e}^2} \tag{C.32}$$

In the limit in which $\epsilon\to 0$, the entanglement is maximum $E=1=\lim_{d\to\infty}(1-\frac{1}{d})$.

We finally compute the expression for the exponential average:

$$\langle \mathrm{e}^{-\beta_1 W}\rangle_{\rho_\mathrm{e}}=\frac{m_1+m_2}{\sqrt{m_1^2-2m_1m_2+m_2\left(m_2-4m_1\frac{\sigma_1^2}{\Delta_1^2}\right)-\frac{4\beta_1^2\sigma_1^2\sigma_2^2\left(\frac{\sigma_1^2}{\Delta_1^2}+1\right)}{\frac{4\mathrm{e}^2\sigma_1^2\sigma_2^2}{\hbar^2}+\frac{\sigma_1^2}{\Delta_1^2}+1}}}. \tag{C.33}$$

With $\frac{\sigma_1}{\Delta_1} = \epsilon$, $\vartheta_{\mathfrak{e}} = \hbar/(2\mathfrak{e}\sigma_1\sigma_2)$, and $\epsilon \to 0$, we have

$$\langle \mathrm{e}^{-\beta_1 W} \rangle_{\rho_{\mathfrak{e}}} \cong \frac{m_1 + m_2}{\sqrt{(m_1 - m_2)^2 - \frac{\hbar^2\beta_1^2}{\mathfrak{e}^2(1+\vartheta_{\mathfrak{e}}^2)}}}, \tag{C.34}$$

C.4 Classically correlated case

Now we consider the classically correlated state

$$\rho_{\mathfrak{c}} = \int \mathrm{d}p \, \frac{\mathrm{e}^{-\frac{p^2}{2\Delta_1^2}}}{\sqrt{2\pi\Delta_1^2}} G_{(0,p),\sigma_1} \otimes G_{(\mathfrak{c}p,0),\sigma_2} \tag{C.35}$$

which has the same form as ρ_c in (6.33), but here the momentum of particle 1 is classically correlated with the position (instead of the momentum) of particle 2 through the parameter $\mathfrak{c}$. The reduced states are exactly deduced as

$$\rho_1 = \mathrm{Tr}_2(\rho_{\mathfrak{c}}) = T_{\Delta_1}(\sigma_1) \tag{C.36}$$

and

$$\rho_2 = \mathrm{Tr}_1(\rho_{\mathfrak{c}}) = \frac{1}{\mathcal{Z}_{m_1}^{\beta}} \int_{-\infty}^{\infty} dp \, \mathrm{e}^{-\frac{\beta p^2}{2m_1}} G_{(\mathfrak{c}p,0),\sigma_2}. \tag{C.37}$$

ρ_1 then approach a thermal state with inverse temperature β_1, in the limit $\frac{\sigma_1}{\Delta_1} = \epsilon \to 0$. The reduced state ρ_2 can be thought to be a Gaussian-weighted mixture in the position basis. To check that, we notice that

$$\langle x_2' | \, \rho_2 \, | x_2 \rangle = \frac{\exp\left[-\frac{\sigma_2^2(x_2 - x_2')^2}{2\hbar^2(1+\vartheta_{\mathfrak{c}}^2\epsilon^2)} - \frac{\left(x_2^2 + x_2'^2\right)}{4\Delta_1^2(1+\vartheta_{\mathfrak{c}}^2\epsilon^2)} \right]}{\sqrt{2\pi\Delta_{\mathfrak{c}}^2\left(1 + \vartheta_{\mathfrak{c}}^2\epsilon^2\right)}}, \tag{C.38}$$

where we defined $\Delta_{\mathfrak{c}} = \mathfrak{c}\Delta_1$, $\vartheta_{\mathfrak{c}} = \hbar/(2\mathfrak{c}\sigma_1\sigma_2)$, and therefore $\hbar/(2\sigma_2\Delta_{\mathfrak{c}}) = \vartheta_{\mathfrak{c}}\epsilon$. In the limit of bounded $\vartheta_{\mathfrak{c}}$ and $\epsilon \to 0$, it follows that

$$\begin{aligned} \langle x_2 | \, \rho_2 \, | x_2 \rangle &\to \frac{1}{\sqrt{2\pi\Delta_{\mathfrak{c}}^2}} \exp\left[-\frac{x^2}{2\Delta_{\mathfrak{c}}^2} \right] \\ \langle x_2' | \, \rho_2 \, | x_2 \rangle &\to 0 \quad \text{if} \quad x_2' \neq x_2. \end{aligned} \tag{C.39}$$

We compute exactly, for state $\rho_{\mathfrak{c}}$, the following expression:

$$\langle \mathrm{e}^{-\beta_1 W} \rangle_{\rho_{\mathfrak{c}}} = \frac{m_1 + m_2}{\sqrt{-4\beta_1^2\sigma_1^2\sigma_2^2 + (m_1 - m_2)^2 - 4\beta_1 m_2 \sigma_1^2}}. \tag{C.40}$$

so that, when $\frac{\sigma_1}{\Delta_1} = \epsilon$, $\vartheta_{\mathfrak{c}} = \hbar/(2\mathfrak{c}\sigma_1\sigma_2)$ and $\epsilon \to 0$, we obtain

$$\langle \mathrm{e}^{-\beta_1 W} \rangle_{\rho_{\mathfrak{c}}} \cong \frac{m_1 + m_2}{\sqrt{(m_1 - m_2)^2 - \frac{\hbar^2\beta_1^2}{\mathfrak{c}^2\vartheta_{\mathfrak{c}}^2}}}. \tag{C.41}$$

C.5 TPM and Entanglement

The Two Point Measurement (TPM) protocol constitutes an alternative view of raising work statistics commonly adopted in contexts involving an external driving parameter $\lambda(t)$, as we discussed in Section 2.5.2. We show here that, an adaptation of this protocol, to our mechanical perspective, may lead to a suppression of the effect of the entanglement effects, described in Eq. (C.24).

As it can be checked in the Heisenberg solution Eq. (6.22), the kinetic energy operator K_1 of particle 1 commutes for both times 0 and $v\tau$ (see Eq. (6.23)), so that given that the work expression is written as $W = K_1(v\tau) - K_1(0)$, with $[K_1(v\tau), K_1(0)]$. Therefore, it might be expected [31] that work observable statistics, which we have raised until now, may coincide with TPM predictions. However, it turns out that for the entangled state $\rho_{\mathfrak{e}}$, this prediction cannot be verified, since the first measurement of a TPM protocol cancels out the quantum correlation term in the first measurement. This fact can be verify directly computing the probability density $\wp_{p_i}$ of a momentum p_i, and therefore a kinetic energy $p_i^2/2m_1$, to be obtained in the first measurement:

$$\wp_{p_i} = \mathrm{Tr}\left(\left(|p_1\rangle\langle p_1| \otimes \mathbb{1}_2\right)\rho_{\mathfrak{e}}\right) = \frac{1}{\sqrt{2\pi(\Delta_1^2+\sigma_1^2)}}\exp\left[-\frac{p_i^2}{2(\sigma_1^2+\Delta_1^2)}\right] \tag{C.42}$$

After the first measurement, the state of the system can be taken to be approximately $G_{(0,p),\sigma_1} \otimes G_{(\mathfrak{c}p,0),\sigma_2}$, with sufficiently low σ_1. However, considering the same procedure for the classically correlated state $\rho_{\mathfrak{c}}$, we deduce that the density probability of the first measurement is the same,

$$\wp_{p_i} = \mathrm{Tr}\left(\left(|p_1\rangle\langle p_1| \otimes \mathbb{1}_2\right)\rho_{\mathfrak{c}}\right) = \frac{1}{\sqrt{2\pi(\Delta_1^2+\sigma_1^2)}}\exp\left[-\frac{p_i^2}{2(\sigma_1^2+\Delta_1^2)}\right] \tag{C.43}$$

and after this measurement, it is reasonable to take the state as again approximately $G_{(0,p),\sigma_1} \otimes G_{(\mathfrak{c}p,0),\sigma_2}$. Therefore, the density probability related to the first measurement for both $\rho_{\mathfrak{e}}$ and $\rho_{\mathfrak{c}}$ is the same and the state right after it, will also coincide, so that the TPM statistics cannot be distinct for both $\rho_{\mathfrak{e}}$ and $\rho_{\mathfrak{c}}$. As a result, a relation like (C.34) cannot be attained using TPM protocol, even though the energies in the beginning and end of the interval commutes.

D Results of Section 7.3

In the present appendix, we aim to deduce the main results of Section 7.3. We consider the energy operator described for any time t in a Heisenberg picture as in Eq. (D.2), rewritten here as:

$$E_{\mathrm{S}}(t) \equiv E_{\mathrm{S}} = \sum_{i,j=1}^{N} \sum_{n_i,n_j} c_{ij}^{n_i n_j} A_i^{n_i} A_j^{n_j}. \tag{D.1}$$

Its time derivative can be written as

$$\dot{E}_{\mathrm{S}} = \sum_{j=1}^{N} \mathcal{L}_j\left(\dot{A}_j\right) \tag{D.2}$$

where $\mathcal{L}_j(\cdot)$ are superoperators acting in the operator space and, according to the product rule, for any operator A_j of the family $\{A_i\}_{i=1}^{N}$, we have to

$$\mathcal{L}_j\left(\dot{A}_j\right) = \sum_{i=1}^{N} \sum_{n_i,n_j} c_{ij}^{n_i n_j} A_i^{n_i} \sum_{k=0}^{n_j-1} A_j^{k}\left(\dot{A}_j\right) A_j^{n_j-k-1} + \sum_{l=1}^{N} \sum_{n_j,n_l} c_{jl}^{n_j n_l} \sum_{k=0}^{n_j-1} A_j^{k}\left(\dot{A}_j\right) A_j^{n_j-k-1} A_l^{n_l}. \tag{D.3}$$

Besides, if some operators A_i in the expression (D.2) are replaced by operators $\langle A_i \rangle \mathbb{1} \equiv \langle A_i(t) \rangle \mathbb{1} \equiv a_i \mathbb{1}$, then the energy operator resulting from E_{S} after the substitutions is represented by $E_{\mathrm{S}}^{\mathfrak{C}}$ where $\mathfrak{C}$ is a index set containing all the indexes of every operator i substituted $A_i \to a_i \mathbb{1}$. With E_{S} in the form (D.1), then we have that

$$\begin{aligned} E_{\mathrm{S}}^{\mathfrak{C}} &= \textstyle\sum_{i,j\in\mathfrak{C}} \sum_{n_i,n_j} c_{ij}^{n_i n_j} a_i^{n_i}(t') a_j^{n_j}(t') + \sum_{i\in\mathfrak{C}, j\notin\mathfrak{C}} \sum_{n_i,n_j} c_{ij}^{n_i n_j} a_i^{n_i}(t') A_j^{n_j} + \\ &+ \textstyle\sum_{i\notin\mathfrak{C} j\in\mathfrak{C}} \sum_{n_i,n_j} c_{ij}^{n_i n_j} A_i^{n_i} a_j^{n_j}(t') + \sum_{i\notin\mathfrak{C} j\notin\mathfrak{C}} \sum_{n_i,n_j} c_{ij}^{n_i n_j} A_i^{n_i} A_j^{n_j}(t') \end{aligned} \tag{D.4}$$

and the respective time derivative can be written as

$$\dot{E}_{\mathrm{S}}^{\mathfrak{C}} = \sum_{j\in\mathfrak{C}} \mathcal{L}_j^{\mathfrak{C}}\left(\dot{a}_j \mathbb{1}\right) + \sum_{j\notin\mathfrak{C}} \mathcal{L}_j^{\mathfrak{C}}\left(\dot{A}_j\right) \tag{D.5}$$

where

$$\begin{aligned} \mathcal{L}_j^{\mathfrak{C}}\left(\dot{A}_j\right) &= \sum_{i\in\mathfrak{C}} \sum_{n_i,n_j} c_{ij}^{n_i n_j} a_i^{n_i} \sum_{k=0}^{n_j-1} A_j^{k}\left(\dot{A}_j\right) A_j^{n_j-k-1} + \\ &+ \sum_{l\in\mathfrak{C}} \sum_{n_j,n_l} c_{jl}^{n_j n_l} \sum_{k=0}^{n_j-1} A_j^{k}\left(\dot{A}_j\right) A_j^{n_j-k-1} a_l^{n_l} \\ &+ \sum_{i\notin\mathfrak{C}} \sum_{n_i,n_j} c_{ij}^{n_i n_j} A_i^{n_i} \sum_{k=0}^{n_j-1} A_j^{k}\left(\dot{A}_j\right) A_j^{n_j-k-1} \\ &+ \sum_{l\notin\mathfrak{C}} \sum_{n_j,n_l} c_{jl}^{n_j n_l} \sum_{k=0}^{n_j-1} A_j^{k}\left(\dot{A}_j\right) A_j^{n_j-k-1} A_l^{n_l} \end{aligned} \tag{D.6}$$

With these properties in mind, we are therefore in a position to deduce the following Theorem:

Theorem D.1. *Assume that hypotheses (H1) and (H2) of Section 7.3 are satisfied. Also, consider that some of the operators A_i, $i \in \mathfrak{E}$ are ϵ-FOs, so that*

$$\frac{\sigma_{A_i}}{s_{\mathscr{A}_i}} \leq \epsilon, \quad \textit{and} \quad \frac{\sigma_{\dot{A}_i}}{s_{\mathscr{A}_i}} \leq \epsilon, \tag{D.7}$$

where $s_{\mathscr{A}_i}$ and $s_{\mathscr{A}_i}$ are scale factors defined in Chapter 7. It follows then that

$$\left|\left\langle \dot{E}_{\mathrm{S}} \right\rangle - \left\langle \dot{E}_{\mathrm{S}}^{\mathfrak{E}} \right\rangle\right| \leq C\epsilon \tag{D.8}$$

where C is a positive real constant. Consequently, if for every $i \in \mathfrak{E}$, the following condition is satisfied

$$\frac{\sigma_{A_i}}{s_{\mathscr{A}_i}} \to 0 \qquad \textit{and} \qquad \frac{\sigma_{\dot{A}_i}}{s_{\mathscr{A}_i}} \to 0, \tag{D.9}$$

then

$$\left|\left\langle \dot{E}_{\mathrm{S}} \right\rangle - \left\langle \dot{E}_{\mathrm{S}}^{\mathfrak{E}} \right\rangle\right| \to 0 \tag{D.10}$$

and $\left\langle \dot{E}_{\mathrm{S}} \right\rangle \to \left\langle \dot{E}_{\mathrm{S}}^{\mathfrak{E}} \right\rangle$.

Proof. We begin the proof by showing that

$$\left|\left\langle \mathcal{L}_j\left(\dot{A}_j\right) - \mathcal{L}_j^{\mathfrak{E}}\left(\dot{A}_j\right) \right\rangle\right| \leq C_j'\epsilon \quad j \notin \mathfrak{E}. \tag{D.11}$$

and

$$\left|\left\langle \mathcal{L}_j\left(\dot{A}_j\right) - \mathcal{L}_j^{\mathfrak{E}}\left(\dot{a}_j\right) \right\rangle\right| \leq C_j''\epsilon \quad j \in \mathfrak{E}, \tag{D.12}$$

and then we prove the result (D.8). Considering Eqs. (D.3) and (D.6), we note that

$$\begin{aligned} \mathcal{L}_j\left(\dot{A}_j\right) - \mathcal{L}_j^{\mathfrak{E}}\left(\dot{A}_j\right) &= \sum_{i\in\mathfrak{E}}\sum_{n_i,n_j} c_{ij}^{n_i n_j}\left(A_i^{n_i} - a_i^{n_i}\right)\left(\sum_{k=0}^{n_j-1} A_j^k\left(\dot{A}_j\right) A_j^{n_j-k-1}\right) \\ &+ \sum_{l\in\mathfrak{E}}\sum_{n_j,n_l} c_{jl}^{n_j n_l}\left(\sum_{k=0}^{n_j-1} A_j^k\left(\dot{A}_j\right) A_j^{n_j-k-1}\right)\left(A_l^{n_l} - a_l^{n_l}\right) \end{aligned} \tag{D.13}$$

and

$$\begin{aligned} \left|\left\langle \mathcal{L}_j\left(\dot{A}_j\right) - \mathcal{L}_j^{\mathfrak{E}}\left(\dot{A}_j\right) \right\rangle\right| &\leq \sum_{i\in\mathfrak{E}}\sum_{n_i,n_j}\sum_{k=0}^{n_j-1} |c_{ij}^{n_i n_j}| \left|\left\langle \left(A_i^{n_i} - a_i^{n_i}\right) A_j^k \dot{A}_j A_j^{n_j-k-1} \right\rangle\right| + \\ &+ \sum_{l\in\mathfrak{E}}\sum_{n_j,n_l}\sum_{k=0}^{n_j-1} |c_{jl}^{n_j n_l}| \left|\left\langle A_j^k \dot{A}_p A_j^{n_j-k-1}\left(A_l^{n_l} - a_l^{n_l}\right) \right\rangle\right|. \end{aligned} \tag{D.14}$$

Now, let us examine the terms within the summation. First, we look at the sum of i:

$$\begin{aligned} \left|\left\langle \left(A_i^{n_i} - a_i^{n_i}\right) A_p^k \dot{A}_j A_j^{n_j-k-1} \right\rangle\right| &= \left|\left\langle \left(A_i^{n_i} - A_i^{n_i-1}a_i + A_i^{n_i-1}a_i - a_i^{n_i}\right) A_j^k \dot{A}_j A_j^{n_j-k-1} \right\rangle\right| \\ &\leq \left|\left\langle \left(A_i - a_i\right) A_i^{n_i-1} A_j^k \dot{A}_j A_j^{n_j-k-1} \right\rangle\right| + \\ &+ \left|\left\langle \left(A_i^{n_i-1}a_i - a_i^{n_i}\right) A_j^k \dot{A}_j A_j^{n_j-k-1} \right\rangle\right|. \end{aligned} \tag{D.15}$$

From the Cauchy-Schwartz theorem, and the definition of ϵ-FOs, we have that

$$\begin{aligned}\left|\left\langle (A_i - a_i)\, A_i^{n_i-1} A_j^k \dot{A}_j A_j^{n_j-k-1} \right\rangle\right| &\leq \sqrt{\left\langle (A_i - a_i)^2 \right\rangle} \sqrt{\left\langle \left(A_i^{n_i-1} A_j^k \dot{A}_j A_j^{n_j-k-1} \right)^2 \right\rangle} \\ &\leq C_{1ij}\epsilon\end{aligned} \tag{D.16}$$

where

$$C_{1ij} = \sqrt{\left\langle \left(A_i^{n_i-1} A_j^k \dot{A}_j A_j^{n_j-k-1} \right)^2 \right\rangle} |s_{\mathscr{A}_i}|. \tag{D.17}$$

Consequently,

$$\begin{aligned}\left|\left\langle \left(A_i^{n_i} - a_i^{n_i}\right) A_j^k \dot{A}_j A_j^{n_j-k-1} \right\rangle\right| &\leq C_{1ij}\epsilon + \left|\left\langle \left(A_i^{n_i-1} a_i - a_i^{n_i} \right) A_p^k \dot{A}_p A_p^{n_p-k-1} \right\rangle\right| \\ &\leq C_{1ij}\epsilon + |a_i| \left|\left\langle \left(A_i^{n_i-1} - a_i^{n_i-1} \right) A_p^k \dot{A}_p A_p^{n_p-k-1} \right\rangle\right|.\end{aligned} \tag{D.18}$$

Considering a similar process, we get

$$\left|\left\langle \left(A_i^{n_i-1} - a_i^{n_i-1} \right) A_p^k \dot{A}_p A_p^{n_p-k-1} \right\rangle\right| \leq C_{2ij}\epsilon + |a_i| \left|\left\langle \left(A_i^{n_i-2} - a_i^{n_i-2} \right) A_p^k \dot{A}_p A_p^{n_p-k-1} \right\rangle\right| \tag{D.19}$$

with

$$C_{2ij} = \sqrt{\left\langle \left(A_i^{n_i-2} A_j^k \dot{A}_j A_j^{n_j-k-1} \right)^2 \right\rangle} |s_{\mathscr{A}_i}|. \tag{D.20}$$

By induction, therefore, we have

$$\left|\left\langle \left(A_i^{n_i} - a_i^{n_i}\right) A_j^k \dot{A}_j A_j^{n_j-k-1} \right\rangle\right| \leq \epsilon \sum_{q=1}^{n_i} C_{qij} |a_i|^{q-1} \tag{D.21}$$

where

$$C_{qij} = \sqrt{\left\langle \left(A_i^{n_i-q} A_j^k \dot{A}_j A_j^{n_j-k-1} \right)^2 \right\rangle} |s_{\mathscr{A}_i}|. \tag{D.22}$$

According to hypothesis (H2), C_{qij} must be bounded by a real constant. Likewise, it can be deduced that

$$\left|\left\langle A_j^k \dot{A}_j A_j^{n_j-k-1} \left(A_l^{n_l} - a_l^{n_l}\right) \right\rangle\right| \leq \epsilon \sum_{q'=1}^{n_l} C'_{q'jl} |a_l|^{q'-1} \tag{D.23}$$

where

$$C'_{q'ij} = \sqrt{\left\langle \left(A_j^k \dot{A}_j A_j^{n_j-k-1} A_i^{n_l-q'} \right)^2 \right\rangle} |s_{\mathscr{A}_l}|. \tag{D.24}$$

Inserting these results into Eq. (D.14), we have

$$\begin{aligned}\left|\left\langle \mathcal{L}_j\left(\dot{A}_j\right) - \mathcal{L}_j^{\mathfrak{E}}\left(\dot{A}_j\right) \right\rangle\right| \leq \epsilon \Bigg(&\sum_{i\in\mathfrak{E}} \sum_{n_i,n_j} \sum_{k=0}^{n_j-1} |c_{ij}^{n_i n_j}| \sum_{q=1}^{n_i} C_{qij} |a_i|^{q-1} + \\ &+ \sum_{l\in\mathfrak{E}} \sum_{n_j,n_l} \sum_{k=0}^{n_j-1} |c_{jl}^{n_j n_l}| \sum_{q'=1}^{n_l} C'_{q'jl} |a_l|^{q'-1} \Bigg)\end{aligned} \tag{D.25}$$

such that

$$\left|\left\langle \mathcal{L}_j\left(\dot{A}_j\right)-\mathcal{L}_j^{\mathfrak{E}}\left(\dot{A}_j\right)\right\rangle\right| \leq C_j'\epsilon \tag{D.26}$$

where

$$C_j'=\left(\sum_{i\in\mathfrak{E}}\sum_{n_i,n_j}\sum_{k=0}^{n_j-1}|c_{ij}^{n_in_j}|\sum_{q=1}^{n_i}C_{qij}|a_i|^{q-1}+\sum_{l\in\mathfrak{E}}\sum_{n_j,n_l}\sum_{k=0}^{n_j-1}|c_{jl}^{n_jn_l}|\sum_{q'=1}^{n_l}C'_{q'jl}|a_l|^{q'-1}\right) \tag{D.27}$$

From hypothesis (H2), C_{qjl} and $C'_{q'jl}$ are limited, and, additionally, $|c_{ij}^{n_in_j}|\to 0$ with $n_i\to\infty$ or $n_j\to\infty$, so C_j' is expected to be bounded.

To deduce

$$\left|\left\langle \mathcal{L}_j\left(\dot{A}_j\right)-\mathcal{L}_j^{\mathfrak{E}}\left(\dot{a}_j\right)\right\rangle\right| \leq C_j''\epsilon, \tag{D.28}$$

as described in Eq. (D.12), we start with the following inequality:

$$\left|\left\langle \mathcal{L}_j\left(\dot{A}_j\right)-\mathcal{L}_j^{\mathfrak{E}}\left(\dot{a}_j\right)\right\rangle\right| \leq \left|\left\langle \mathcal{L}_j\left(\dot{A}_j\right)-\mathcal{L}_j^{a_j}\left(\dot{a}_j\right)\right\rangle\right|+\left|\left\langle \mathcal{L}_j^{a_j}\left(\dot{a}_j\right)-\mathcal{L}_j^{\mathfrak{E}}\left(\dot{a}_j\right)\right\rangle\right| \tag{D.29}$$

where we add and subtract $\mathcal{L}_j^{a_j}$, resultant from the substitution $A_j\to a_j$ and $\dot{A}_j\, rightarrow\dot{a}_j$ in $\mathcal{L}_j\left(\dot{A}_j\right)$. The expression

$$\left|\left\langle \mathcal{L}_j^{a_j}\left(\dot{A}_j\right)-\mathcal{L}_j^{\mathfrak{E}}\left(\dot{a}_j\right)\right\rangle\right| \tag{D.30}$$

is simply the result of replacing $A_j\to a_j$ and $\dot{A}_j\to\dot{a}_j$ in Eq. (D.26), so that

$$\left|\left\langle \mathcal{L}_j^{a_j}\left(\dot{a}_j\right)-\mathcal{L}_j^{\mathfrak{E}}\left(\dot{a}_j\right)\right\rangle\right| \leq C_j^{'a_j}\epsilon \tag{D.31}$$

where

$$C_j^{'a_j}=C_j'\left(A_j\to a_j\right). \tag{D.32}$$

On the other hand, in an inductive process similar to the one used to deduce (D.26), we can obtain

$$\begin{aligned}\left|\left\langle A_i^{n_i}\left(A_j^kA_j^{n_j-k-1}-a_j^k\dot{a}_ja_j^{n_j-k-1}\right)\right\rangle\right| \leq \epsilon\Bigg(&\sum_{q=1}^{n_j-k-1}D_{iq}|a_j|^{q-1}+|a_j|^{n_j-k-1}|F_i\\&+|a_j|^{n_j-k-1}|\dot{a}_j|\left(\sum_{q'=1}^{k}E_{iq'}|a_j|^{q'-1}\right)\Bigg)\end{aligned} \tag{D.33}$$

and

$$\begin{aligned}\left|\left\langle \left(A_j^kA_j^{n_j-k-1}-a_j^k\dot{a}_ja_j^{n_j-k-1}\right)A_l^{n_l}\right\rangle\right| \leq \epsilon\Bigg(&\sum_{q=1}^{k}D'_{ql}\epsilon|a_j|^{q-1}+|a_j|^k|F'_l\epsilon+\\&+|a_j|^k|\dot{a}_j|\left(\sum_{q'=1}^{n_j-k-1}E'_{q'l}\epsilon|a_j|^{q'-1}\right)\Bigg)\end{aligned} \tag{D.34}$$

where

$$D_{iq} = \sqrt{\left\langle \left(A_i^{n_i} A_j^k \dot{A}_j A_j^{n_j-k-1-q} \right)^2 \right\rangle} |a_{j,S}|, \quad F_i = \sqrt{\left\langle \left(A_i^{n_i} A_j^k \right)^2 \right\rangle} |\dot{a}_{j,S}|,$$
$$E_{iq'} = \sqrt{\left\langle \left(A_i^{n_i} A_j^{k-q'} \right)^2 \right\rangle} |a_{j,S}|, \quad D'_{ql} = \sqrt{\left\langle \left(A_j^{k-q'} \dot{A}_j A_j^{n_j-k-1} A_l^{n_l} \right)^2 \right\rangle} |a_{j,S}|,$$
$$F'_l = \sqrt{\left\langle \left(A_j^{n_j-k-1} A_l^{n_l} \right)^2 \right\rangle} |\dot{a}_{j,S}|, \quad E'_{q',l} = \sqrt{\left\langle \left(A_j^{n_j-k-1-q'} A_l^{n_l} \right)^2 \right\rangle} |a_{j,S}|. \tag{D.35}$$

From the results (D.31), (D.33), and (D.34), we have that

$$\left| \left\langle \mathcal{L}_j \left(\dot{A}_j \right) - \mathcal{L}_j^{\mathfrak{E}} \left(\dot{a}_j \right) \right\rangle \right| \leq C''_j \epsilon \tag{D.36}$$

where

$$\begin{aligned} C''_j = & \\ \leq & \sum_{i=1}^{N} \sum_{n_i,n_j} \sum_{k=0}^{n_j-1} |c_{ij}^{n_i n_j}| \left(\sum_{q=1}^{n_j-k-1} D_{iq} |a_j|^{q-1} + |a_j|^{n_j-k-1} |F_i + |a_j|^{n_j-k-1} |\dot{a}_j| \left(\sum_{q'=1}^{k} E_{iq'} |a_j|^{q'-1} \right) \right) + \\ & + \sum_{l=1}^{N} \sum_{n_j,n_l} \sum_{k=0}^{n_j-1} |c_{jl}^{n_j n_l}| \left(\sum_{q=1}^{k} D'_{ql} |a_j|^{q-1} + |a_j|^k |F'_l + |a_j|^k |\dot{a}_j| \left(\sum_{q'=1}^{n_j-k-1} E'_{q'l} |a_j|^{q'-1} \right) \right) + C_j'^{a_j} \end{aligned} \tag{D.37}$$

From Hypothesis (H2), C''_j is bounded as well.

Finally, considering Eqs. (D.26) and (D.36), we prove the results (D.11) and (D.12), getting

$$\begin{aligned} \left| \langle \dot{E}_S \rangle - \left\langle \dot{E}_S^{\mathfrak{E}} \right\rangle \right| & \leq \sum_{j \in \mathfrak{E}} \left| \left\langle \mathcal{L}_j \left(\dot{A}_j \right) - \mathcal{L}_j^{\mathfrak{E}} \left(\dot{a}_j \right) \right\rangle \right| + \sum_{j \notin \mathfrak{E}} \left| \left\langle \mathcal{L}_j \left(\dot{A}_j \right) - \mathcal{L}_j^{\mathfrak{E}} \left(\dot{A}_j \right) \right\rangle \right| \\ & \leq C\epsilon \end{aligned} \tag{D.38}$$

where, since C'_j and C''_j are bounded, then there is a positive real scalar C such that

$$C \geq \sum_{j \in \mathfrak{E}} C''_j + \sum_{j \notin \mathfrak{E}} C'_j. \tag{D.39}$$

In the limit $\epsilon \to 0$, we deduce that

$$\left| \langle \dot{E}_S \rangle - \left\langle \dot{E}_S^{\mathfrak{E}} \right\rangle \right| \to 0, \tag{D.40}$$

since C is bounded. □

Note that $E_S^{\mathfrak{E}}$ will usually have its Schrödinger version $\left(E_S^{\mathfrak{E}}\right)^{\mathfrak{s}} = U_t E_S^{\mathfrak{E}} U_t^\dagger$ as an operator explicitly dependent on the time. Notably, from Eq. (D.4), and, given that the dynamics is unitary, we have that

$$\begin{aligned} \left(E_S^{\mathfrak{E}} \right)^S & = \sum_{i,j \in \mathfrak{E}} \sum_{n_i,n_j} c_{ij}^{n_i n_j} a_i^{n_i}(t') a_j^{n_j}(t') + \sum_{i \in \mathfrak{E}, j \notin \mathfrak{E}} \sum_{n_i,n_j} c_{ij}^{n_i n_j} a_i^{n_i}(t') (A_j^{n_j})^S + \\ & + \sum_{i \notin \mathfrak{E} j \in \mathfrak{E}} \sum_{n_i,n_j} c_{ij}^{n_i n_j} \left(A_i^{n_i} \right)^S a_j^{n_j}(t') \end{aligned} \tag{D.41}$$

where, since A_i are not explicitly time-dependent operators (see hypothesis (H1)), $\left(A_i^{n_i}\right)^S = U_t A_i^{n_i} U_t^\dagger = \left(A_i^S\right)^{n_i}$. In this way, it can be deduced that

$$\partial_t \left(E_S^{\mathfrak{E}}\right)^S = \sum_{j\in\mathfrak{E}} U_t(\mathcal{L}_j^{\mathfrak{E}}\left(\dot{a}_j\mathbb{1}\right))U_t^\dagger \tag{D.42}$$

Therefore, from a Heisenberg picture, we have

$$\dot{E}_S^{\mathfrak{E}} = \frac{1}{i\hbar}\left[E_S^{\mathfrak{E}}, H\right] + U_t^\dagger\left(\partial_t\left(E_S^{\mathfrak{E}}\right)^S\right)U_t, \tag{D.43}$$

and, from Eqs. (D.42) and (D.5),

$$\frac{1}{i\hbar}\left[E_S^{\mathfrak{E}}, H\right] = \sum_{j\notin\mathfrak{E}} \mathcal{L}_j^{\mathfrak{E}}\left(\dot{A}_j\right) \tag{D.44}$$

As a consequence, we can prove the following Corollary of the Theorem D.1:

Corollary D.1. *Consider the same assumptions of theorem D.1. Furthermore, consider that the Schrödinger version $\left(E_S^{\mathfrak{E}}\right)^S$ acts only on the Hilbert space of the system of interest $\mathbb{H}_S$. So it follows that*

$$\left|\left\langle\dot{E}_S\right\rangle - \left(\mathrm{Tr}_S\left[\rho_S(t)\partial_t\left(E_S^{\mathfrak{E}}\right)^S\right] + \mathrm{Tr}_S\left[\partial_t\rho_S(t)\left(E_S^{\mathfrak{E}}\right)^S\right]\right)\right| \leq C\epsilon \tag{D.45}$$

and

$$\mathrm{Tr}_S\left[\rho_S(t)\partial_t\left(E_S^{\mathfrak{E}}\right)^S\right] = \mathrm{Tr}\left[\rho\left(\sum_{j\in\mathfrak{E}}^N \mathcal{L}_j^{\mathfrak{E}}\left(\dot{a}_j\right)\right)\right], \tag{D.46}$$

$$\mathrm{Tr}_S\left[\rho_S(t)\left(E_S^{\mathfrak{E}}\right)^S\right] = \mathrm{Tr}\left[\rho\left(\sum_{j\notin\mathfrak{E}}^N \mathcal{L}_j^{\mathfrak{E}}\left(\dot{A}_j\right)\right)\right], \tag{D.47}$$

where C is a real positive constant and $\rho_S(t)$ and Tr_S refers to the reduced density operator, resulting from the partial trace of degrees of external to S, and the trace only in the degrees of freedom of S, respectively. As a consequence,

$$\lim_{\epsilon\to 0}\left\langle\dot{E}_S\right\rangle = \mathrm{Tr}_S\left[\rho_S(t)\partial_t\left(E_S^{\mathfrak{E}}\right)^S\right] + \mathrm{Tr}_S\left[\partial_t\rho_S(t)\left(E_S^{\mathfrak{E}}\right)^S\right]. \tag{D.48}$$

Proof. Since the Corollary Hypothesis encompasses those of the Theorem D.1, then it is only necessary to prove Eqs. (D.46) and (D.47). In fact, the results of the Theorem can be written simply by substituting the right side of Eqs. (D.46) and (D.47) in (D.45). From Eq. (D.42), and the fact that $\left(E_S^{\mathfrak{E}}\right)^S$ acts on S,

$$\begin{aligned}
\mathrm{Tr}\left[\rho\left(\textstyle\sum_{j\in\mathfrak{E}}^N \mathcal{L}_j^{\mathfrak{E}}\left(\dot{a}_j\right)\right)\right] &= \mathrm{Tr}\left[\rho\left(U_t^\dagger\partial_t\left(E_S^{\mathfrak{E}}\right)^S U_t\right)\right] \\
&= \mathrm{Tr}_E\,\mathrm{Tr}_S\left[\rho(t)\left(\partial_t\left(E_S^{\mathfrak{E}}\right)^S\right)\right] \\
&= \mathrm{Tr}_S\left[\mathrm{Tr}_E\left(\rho(t)\right)\left(\partial_t\left(E_S^{\mathfrak{E}}\right)^S\right)\right] \\
&= \mathrm{Tr}_S\left[\rho_S(t)\left(\partial_t\left(E_S^{\mathfrak{E}}\right)^S\right)\right]
\end{aligned} \tag{D.49}$$

where E denotes the environment that composes the universe together with S and we consider the definition of reduced density operator (Schröndinger) $\rho_{\mathrm{S}}(t) = \mathrm{Tr}_{\mathrm{E}}(\rho(t))$. On the other hand, from Eq. (D.44), we have

$$\begin{aligned}
\mathrm{Tr}\left[\rho\left(\Sigma_{j\notin\mathfrak{E}}^{N}\mathcal{L}_{j}^{\mathfrak{E}}\left(\dot{A}_{j}\right)\right)\right] &= \mathrm{Tr}\left[\rho\left(U_{t}^{\dagger}\frac{[(E_{\mathrm{S}}^{\mathfrak{E}})^{S},H]}{i\hbar}U_{t}\right)\right] \\
&= \mathrm{Tr}\left[\rho(t)\frac{[(E_{\mathrm{S}}^{\mathfrak{E}})^{S},H]}{i\hbar}\right] \\
&= \mathrm{Tr}\left[\frac{[H,\rho(t)]}{i\hbar}(E_{\mathrm{S}}^{\mathfrak{E}})^{S}\right] \\
&= \mathrm{Tr}_{\mathrm{S}}\,\mathrm{Tr}_{\mathrm{E}}\left[\partial_{t}\rho(t)(E_{\mathrm{S}}^{\mathfrak{E}})^{S}\right] \\
&= \mathrm{Tr}_{\mathrm{S}}\left[\partial_{t}\rho_{\mathrm{S}}(t)\left(E_{\mathrm{S}}^{\mathfrak{E}}\right)^{S}\right]
\end{aligned} \tag{D.50}$$

where we used the von Neumann equation and the cyclic property of the trace. The proof is completed considering the Theorem D.1 with the results (D.49) and (D.50). □

We finally remark here that the results presented in this chapter can be naturally adapted to a non-autonomous inclusive approach.

E Results of Section 7.4

Our aim in the present Appendix is to deduce, under special circumstances, that the fluctuations of the position and velocity of the center of mass are extremely small when compared to the initial length and velocity of the piston. We assume that the average velocity fluctuation of the constituents is constrained, so that:

$$\frac{\sum_{i\in \mathrm{P}} m_i \sigma_{\dot{X}_i}}{\sum_{i\in \mathrm{P}} m_i |\langle \dot{X}_i \rangle|} \leq \frac{1}{\sqrt{N_{\mathrm{P}}}} \tag{E.1}$$

where N_{P} is the total number of particles in the piston[1]. With this consideration, we are now in a position to deduce that the fluctuations in velocity and in the position of the center of mass of the piston are small compared to the average values.

Theorem E.1. *Considering Eq. (E.1), it follows that*

$$\frac{\sigma_{\mathrm{X_{cm}}}(t)}{\int_0^t |\langle \dot{X}_{\mathrm{cm}}(t') \rangle| dt'} \leq \frac{a_{\dot{x}} t + \sigma_{\dot{\mathrm{X}}_{\mathrm{cm}}}(0)}{\int_0^t |\langle \dot{X}_{\mathrm{cm}}(t') \rangle| dt'} \quad e \quad \frac{\sigma_{\dot{\mathrm{X}}_{\mathrm{cm}}}(t)}{\langle \dot{X}_{\mathrm{cm}} \rangle} \leq \frac{a_{\dot{x}}}{\langle \dot{X}_{\mathrm{cm}} \rangle}, \tag{E.2}$$

where $a_{\dot{x}} = (1/\sqrt{N_{\mathrm{P}}}) \frac{\sum_{i\in \mathrm{P}} m_i \langle \dot{X}_i \rangle}{\sum_{i\in \mathrm{P}} m_i} \equiv (1/\sqrt{N_{\mathrm{P}}}) \overline{\langle \dot{X} \rangle}$, *where* $\overline{(\cdot)}$ *denotes the mean value weighted by the mass.*

Proof. Denoting, for any operator A, $\delta A = A - \langle A \rangle$, we can deduce

$$\begin{aligned} \sigma^2_{\dot{\mathrm{X}}_{\mathrm{cm}}} &\equiv \langle \delta^2 \dot{X}_{\mathrm{cm}} \rangle = \tfrac{1}{M_{\mathrm{P}}^2} \textstyle\sum_{i,j\in \mathrm{P}} m_i m_j \langle \dot{X}_i \dot{X}_j \rangle - \tfrac{1}{M_{\mathrm{P}}^2} \textstyle\sum_{i,j\in \mathrm{P}} m_i m_j \langle \dot{X}_i \rangle \langle \dot{X}_j \rangle \\ &= \frac{1}{M_{\mathrm{P}}^2} \sum_{i,j\in \mathrm{P}} m_i m_j \langle \delta \dot{X}_i \delta \dot{X}_j \rangle. \end{aligned} \tag{E.3}$$

From Cauchy-Schwartz theorem, we deduce

$$\begin{aligned} \langle \sigma^2_{\dot{\mathrm{X}}_{\mathrm{cm}}} &= \frac{1}{M_{\mathrm{P}}^2} \sum_{i,j\in \mathrm{P}} m_i m_j \langle \delta \dot{X}_i \delta \dot{X}_j \rangle \leq \frac{1}{M_{\mathrm{P}}^2} \sum_{i,j\in \mathrm{P}} m_i m_j |\langle \delta \dot{X}_i \delta \dot{X}_j \rangle| \\ &\leq \frac{1}{M_{\mathrm{P}}^2} \sum_{i,j\in \mathrm{P}} m_i m_j \sqrt{\langle \delta^2 \dot{X}_i \rangle} \sqrt{\langle \delta^2 \dot{X}_j \rangle}. \end{aligned} \tag{E.4}$$

Taking into account Eq. (E.1):

$$\langle \delta^2 \dot{X}_{\mathrm{cm}} \rangle \leq \frac{1}{M_{\mathrm{P}}^2} \sum_{i,j\in \mathrm{P}} m_i m_j \sqrt{\langle \delta^2 \dot{X}_i \rangle} \sqrt{\langle \delta^2 \dot{X}_j \rangle} = \overline{\langle \delta \dot{X} \rangle}^2 \leq a_{\dot{x}}^2 \tag{E.5}$$

Additionally, it can be deduced that

$$\left| \frac{d}{dt} \sqrt{\langle \delta^2 X_{\mathrm{cm}} \rangle} \right| = \left| \frac{\langle \{ \delta X_{\mathrm{cm}}, \delta \dot{X}_{\mathrm{cm}} \} \rangle}{2 \sqrt{\langle \delta^2 X_{\mathrm{cm}} \rangle}} \right| = \frac{|\langle \{ \delta X_{\mathrm{cm}}, \delta \dot{X}_{\mathrm{cm}} \} \rangle|}{2 \sqrt{\langle \delta^2 X_{\mathrm{cm}} \rangle}} \leq \sqrt{\langle \delta^2 \dot{X}_{\mathrm{cm}} \rangle} \tag{E.6}$$

[1] A common assumption in statistical physics textbooks [18, 40].

Therefore, if initially the state is such that the uncertainty of position is small $\sqrt{\langle \delta^2 X_{\rm cm} \rangle}$, then from Eq. (E.5)

$$\begin{aligned} \sqrt{\langle \delta^2 X_{\rm cm}(t) \rangle} - \sqrt{\langle \delta^2 X_{\rm cm}(0) \rangle} &= \int_0^t \tfrac{d}{dt'} \sqrt{\langle \delta^2 X_{\rm cm}(t') \rangle} dt' \\ &\leq \int_0^t \left| \tfrac{d}{dt} \sqrt{\langle \delta^2 X_{\rm cm}(t') \rangle} \right| dt' \leq a_{\dot{x}} t. \end{aligned} \tag{E.7}$$

Then

$$\frac{\sigma_{X_{\rm cm}}(t)}{\int_0^t |\langle \dot{X}_{\rm cm}(t') \rangle| dt'} \leq \frac{a_{\dot{x}} t + \sigma_{\dot{X}_{\rm cm}}(0)}{\int_0^t |\langle \dot{X}_{\rm cm}(t') \rangle| dt'} \quad \text{e} \quad \frac{\sigma_{\dot{X}_{\rm cm}}(t)}{\langle \dot{X}_{\rm cm} \rangle} \leq \frac{a_{\dot{x}}}{\langle \dot{X}_{\rm cm} \rangle}. \tag{E.8}$$

□

From the theorem, we can conclude that $\frac{a_{\dot{x}}}{\langle \dot{X}_{\rm cm} \rangle} \approx \frac{1}{\sqrt{N_{\rm P}}}$, and with $N_{\rm P} \approx 10^{23}$, then the fluctuation of the position and velocity of the piston's center of mass will be small enough for a long enough time interval.