University of La Laguna

Faculty of Science

Bibliography Revision about Work Fluctuation and a Quantum Simulation of a Symmetry Relation

READ FROM: [1, 2, 3]

Final Degree Project

Author:
Gualberto M. León Cuesta
Tutor:
Daniel Alonso Ramírez

January 2024

"It from bit symbolizes the idea that every item of the physical world has at bottom — at a very deep bottom, in most instances — an immaterial source and explanation; that which we call reality arises in the last analysis from the posing of yes-no questions and the registering of equipment-evoked responses; in short, that all things physical are information-theoretic in origin and that this is a participatory universe."

–John Archibald Wheeler, "Information, Physics, Quantum: The Search for Links" in Complexity, Entropy and the Physics of Information (1990) ed., Wojciech H. Zurek, p. 5.

Acknowledge

Quiero agradecer a mi familia por el apoyo mostrado durante este trabajo, y el transcurso del grado. Sin ellos, nada de esto habría sido posible.

Summary

En este proyecto hemos abordado los fundamentos de la definición del trabajo, desde los conceptos fundamentales de la termodinámica elemental hasta su interpretación probabilística de mucha utilidad en la termodinámica de no equilibrio. Gracias a esta interpretación estadística hemos podido ver que existen una serie de relaciones exactas para el trabajo llamadas teoremas de fluctuación. Donde hemos presentado una de ellas, en concreto la igualdad de Jarzynzky. Con espacial relevancia, ya que nos permite relacionar un funcional del trabajo con magnitudes asociadas a los estados de equilibrio del sistema, independientemente si el procesos es no cuasiestático. La igualdad de Jarzynsky nos permite generalizar la segunda ley de la termodinámica para sistemas fluctuantes, donde esta vez la inigualdad es entre los valores medio del trabajo y la diferencia de energías libres. Siguiendo por esta línea, se han presentado los dos esquemas de medición del trabajo en mecánica cuántica, el esquema en dos tiempos (TTM) y de un tiempo (OTM).

Se ha visto que el esquema TTM consiste en hacer una medida de la energía al principio de un protocolo o proceso termodinámico, y otra al final, y definir el trabajo como la diferencia. Así, bajo este marco, se han presentado los conceptos de función característica y función de distribución de probabilidad del trabajo como transformadas de Fourier una de la otra, que han sido necesarias para realizar una prueba de la igualdad de Jarzynzky para el caso de un sistema cuántico cerrado. Posteriormente se han puesto a prueba los conceptos aprendidos para el experimento de la resonancia magnética, es decir, N espines independientes sujetos a un campo magnético uniforme muy fuerte y una perturbación dependiente del tiempo perpendicular a este. Donde se han discutido las violaciones locales al segundo principio de la termodinámica que se dan para este caso. Que consisten en transiciones de los espines del estado antialineado al campo, al alineado, causadas por la perturbación.

Por otro lado, se ha presentado el esquema OTM. Donde aquí el trabajo también se define como la diferencia de dos medidas de energía, al inicio y al final de protocolo. Salvo que en la segunda se mide un Hamiltoniano condicional donde los estados evolucionados son autoestados de este. Con esto, se consigue que en la segunda medida no se pierdan las coherencias cuánticas debido al proyectar en la base de autoestados del Hamiltoniano final y, por tanto no se pierda la información portada por los estos estados, es por esto que la OTM se considera una TTM no destructiva. Bajo este esquema se ha obtenido una igualdad de Jarzynsky modificada que da cuenta del coste informacional de la medida, al incluir un término que depende de cuán diferente es el estado final del estado térmico de equilibrio al que tendería el sistema después de relajarse. Solucionando la inconsistencia termodinámica que presenta el paradigma de la TTM al no incluir la medida como parte del proceso termodinámico.

Para finalizar se ha visto que la función característica es el puente que nos permite acceder a una prueba experimental del teorema de las fluctuaciones en un ordenador cuántico. Donde la idea fundamental radica en que las operaciones unitarias, es decir, las rotaciones que actuán sobre los estados térmicos pueden ser recreadas en un ordenador cuántico. Donde hemos provisto de una prueba algebraica del porqué podemos calcular la función característica con un circuito cuántico.

Current Status and Scientific Framework

This literature review will deal with fundamental concepts framed within non-equilibrium quantum thermodynamics. Where the results seen are for closed quantum systems and, therefore, the evolution is unitary. Although they may be true for systems weakly coupled to thermal baths, much research is currently being done on open systems [1]. General knowledge about quantum technologies has also been used, such as in one of our reference works [2], as well as basic knowledge of information theory to understand why the difference in information lies in entropy differences.

Throughout the work, we have not seen any systems that exhibit energy dissipation, which is normally the most common except in very controlled environments, and I believe that the next step in understanding the true nature of the work would be to deal with such systems.

Contents

Introduction

In nature, systems that completely overpass our computational and instrumental power, in order to get a full physical characterization, are always present. The instrumental errors in measures on initial conditions could yield, once the system evolves, to very big errors in the final state. This crucial dependence on the initial condition is expressed mathematically by Lyapunov exponents and Lyapunov spectra [4]. This is called chaos and represents the motivation for statistical interpretation of physical phenomena.

In this way, regarding systems with many constituents, we do not study the individual behavior of each component but consider that certain events occur with a given probability. For example, the number of molecules of a gas, enclosed in a container, that collide with the walls of this in a given time; or that cross a certain imaginary surface in a fluid resulting in a net viscous force. This chaotic behavior is modelized by probability densities, thus, all physical quantities obey probability distributions. Some examples are the Maxwell Boltzmann distribution for the velocities of molecules in an ideal gas and the Bose-Einstein and Fermi-Dirac distributions for the occupations of states in bosons and fermions respectively [5]. Then, associated with each physical quantity we will have a deviation concerning a mean value, this is called fluctuation.

Statistical mechanics is the branch of physics that connects these fluctuations with the macroscopic thermodynamic quantities that characterize systems at equilibrium. In such cases, due to the law of large numbers, the mean values of these quantities coincide with the observed macroscopic values. However, this is not always the case, especially when our systems are composed of only a few particles. In other words, there are situations where fluctuations play a fundamental role in the dynamics of these constituents. How it occurs in the spin system of the compound $NaCaNi_2F_7$ [6]. In addition, these fluctuations could introduce local violations of the second principle of thermodynamics [1]. As will be discussed in the following sections for the case of magnetic resonance.

This is why exact relations arise for the work in fast non-equilibrium processes. They are called *fluctuation theorems* and were developed by Jarzynski and Crooks in 1997 and 1998 [7, 8, 9, 10]. These relations can be understood as generalizations of the second law for fluctuating systems [1]. And, they have the power to, no matter the non-equilibrium process we impose on the system, these expressions connect the work on the system with thermodynamic quantities linked to the equilibrium states as if the process had been completely quasi-static. Thus, we will see that it is obtained as a version of the second principle but for the mean values of physical quantities linked to the process. In particular, for work and free energy.

These results have several applications. Among them, they provide insight into the thermodynamic costs of the measurement process in quantum mechanics. In this work, we will discuss the two most widespread quantum mechanical work measurement protocols. The two-time measurement (TTM) scheme and the one-time measurement (OTM) scheme with the particular line of the references [1, 2]. Both are based on the general idea of understanding work as a *random variable*. This interpretation is based on the randomness of the quantum world. Just as when we compress a gas enclosed in a piston, we are faced with pressure and this pressure is due to the exchange of momentum of the molecules as they collide with the walls of the container, which is a random process with a certain probability of collisions in a given time, work will vary from one compression process to another. This difference will be negligible from one realization to another, the greater the number of particles. However, it starts to gain strength when the number of constituents is small.

Let us imagine that we have a quantum system described by a Hamiltonian $\mathcal{H}$ and we vary a parameter λ, so we know its dependence on time, i.e. $\lambda(t)$. This is called a *protocol*. Hence, the most natural way to measure the work would be to take two projections of the energy, one at the beginning and one at the end of the protocol.

The TTM scheme measures two projections of the energy, i.e., the eigenvalues of the Hamiltonian $\mathcal{H}$ at $t = 0$ and at time $t = \tau$ at the end of the protocol. In the second measurement, this method destroys the quantum coherences of the system, causing information to be lost, and is not thermodynamically consistent since it does not take into account the thermodynamic cost of the measurements [3]. This is something that the OTM scheme solves. It consists of a non-destructive TTM in which in the second measurement we do not measure the Hamiltonian at $t = \tau$ but a conditional Hamiltonian defined in the bases of the evolved states. In this way, quantum coherences are maintained. Furthermore, it will be shown that a modified version of the Jarzinsky equality accounts for the informational cost of the measurement in the OTM scheme and solves the thermodynamic inconsistency of the TTM scheme. Finally, there is a symmetry relation deduced from the fluctuation theorems which can be checked by a quantum computer. This relationship appears in the quotient between the forward and backward characteristic functions. Where these characteristic functions can be put as the trace of operators that may or may not be unitary, in any case, a Pauli string decomposition will be applied, and computing this trace will be the same as measuring the Pauli matrix X and Y in a quantum circuit with an ancilla qubit and a thermal target state ρ to which these operators will be applied. This will serve as an experimental test for the fluctuation theorem. Like this one, many other experiments have been proposed to test the reliability of fluctuation theorems, for example, using trapped cold ions [11].

Chapter 1

Work in non-equilibrium Process and Jarzynski Equality

Resumen

En este capítulo introductorio al trabajo en procesos de no equilibrio se recordarán las nociones básicas de la termodinámica elemental, conceptos como, el trabajo, el calor, los procesos isotérmicos y la energía libre de Hemholtz. Se hará hincapié en la definición de proceso cuasiestático. También se utilizará el protocolo de: estado en equilibrio térmico inicial, variación no cuasiestática de un parámetro de trabajo λ hasta un valor final λ_f, relajación hacia un estado de equilibrio cercano y vuelta cuasiestática hasta el estado inicial; para visualizar la segunda ley de la termodinámica y la igualdad de Jarzynsky. Además de, recalcar la importancia de ambas en los procesos de no equilibrio, y dar cuenta de que esta segunda, no prohíbe violaciones locales del segundo principio.

Imagine a physical system in contact with a heat source. In this way, the thermal or internal energy U of the constituents of this system can vary due to the flow of energy between the source and the system. We call this *heat* Q, and the changes produced by external agents that consist in varying certain parameters $\{\lambda_i\}$ that characterize our system are called *work*, W, and the parameters λ_i are called work parameters. Thus, the conservation of energy implies that the internal energy can only be varied by heat flow in the system and by the work done

$$\Delta U = Q + W. \tag{1.1}$$

This is the first law of thermodynamics. From this, we will adopt the convention of $W < 0$ for when the system does work on the surroundings and $W > 0$ for when it is the surroundings that do work on the system.

Elementary thermodynamics studies systems in equilibrium undergoing quasi-static processes. This means that the changes in the parameters of the Hamiltonian $\mathcal{H}$ describing the dynamics of the system are sufficiently slow that at each stage of the process, the system is in equilibrium. In other words, it is as if the process we carry out is sufficiently slow compared to the collisions between constituents or whatever mechanism brings them into contact with each

other, such that the constituents are able to rapidly communicate changes to the other elements of the system, and organize themselves to establish a global macroscopic temperature, pressure, and volume.

For the purpose of this work, *isothermal processes* will always be considered. This means that during the execution of the protocol, the temperature remains constant. Thus, the concept of *Hemholtz free energy* F is of vital importance. "*Free*" because in isothermal processes it is a potential for work in our thermodynamic system. That is,

$$W = \Delta F = \Delta U - Q. \tag{1.2}$$

It is the potential that tells us what part of the energy is free to do work. And later we will see how in non-equilibrium states and for non-quasi-static processes this free energy is a lower bound for non-equilibrium work.

To see this, let us consider that we make a variation of a work parameter λ in such a way that we start from a value λ_i to a value λ_f and we do it quasi-statically, that is, at each moment of the process we have a state of general equilibrium. As we see represented in the figure 1.1 by a dotted line. Thus, the work involved in this process is $W = \Delta F$. Now let's look at the case where we quickly change the working parameter. Without allowing time for the system to adapt to the new conditions. This is represented by a solid line in the figure 1.1. Next, we allow the system to relax to the nearest equilibrium configuration. This is represented by a dashed line up to a state $F(T, \lambda_f)$. In conclusion, the work done to go from point $F(T, \lambda_i)$ to point $F(T, \lambda_f)$ is different from ΔF since the process has not been quasi-static. So, all along the protocol $\lambda(t)$ energy has been used, for example, in irreversible terms such as those of internal heat conduction or those produced if our system were fluid, in terms of friction due to viscosity.

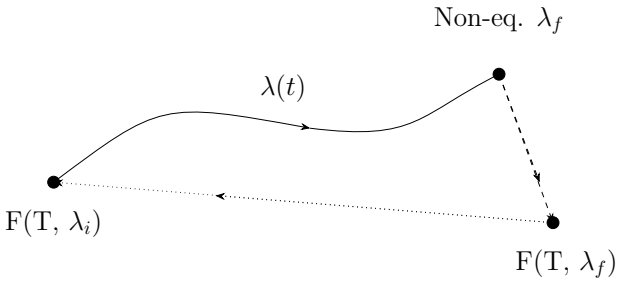


Figure 1.1: Diagram depicting the variations of the working parameter $\lambda(t)$. It represents a protocol that starts with a first step represented by a solid line in which we vary the parameter λ non-quasi-statically. We go from an equilibrium state $F(T, \lambda_i)$ to a non-equilibrium state with a value of λ of λ_f. The next dashed line represents our system relaxing to the equilibrium condition $F(T, \lambda_f)$. And, the dotted line represents the quasi-static process from the final equilibrium position to the initial equilibrium position. This diagram is extracted from reference [1].

This is what the second principle of thermodynamics tells us, that in general for irreversible processes the work done will be greater than ΔF,

$$W \geq \Delta F. \tag{1.3}$$

Or what can be interpreted as a result of Kelvin's statement of the second principle. In that, we cannot extract work from a system, interacting with a single heat source, without altering the state of the system. For example, we can use heat to change the crystalline structure of a material so that it exhibits magnetic properties and we can extract work from that transition, but ultimately we will have altered its initial state. In other words, by thermally interacting with a single component, obtaining work cannot be the only goal.

To visualize this, let us focus on the process schematized in the figure 1.1, where we will call $W_{irreversible}$ the work done in the first step. Then, in the realignment process, since the work parameter does not vary, the work done is zero. And, in the last branch, where the work done is ΔF since it is a quasi-static process. Thus, the balance of the total work done is $W_{outward} + W_{return} = W_{outward} - \Delta F$ And, as the system returns to the same initial state, interacting with a single source of energy, this work must not be negative (which would mean that we would be extracting work). Therefore, $W_{outward} - \Delta F \geq 0$ which is exactly the relation 1.3.

In the next section, we will see how the fluctuation theorems generalize the second principle. Relations will emerge that will bring together the average value of work in non-equilibrium processes with equilibrium quantities.

1.1 The Jarzynski equality

At the beginning of this chapter, we have seen all that elementary thermodynamics understands of this type of non-equilibrium processes, using the inequation 1.3. In this way, we establish a lower bound for the irreversible work from the second principle. However, it is possible to find exact relations, i.e. equalities for work in non-equilibrium processes. These relations are called *fluctuation theorems*. There is a very powerful result within the fluctuation theorems known as Jarzinski's equality, developed in 1997 [7, 8]. Based fundamentally on the interpretation of work as a *random variable*.

This interpretation is quite intuitive. Imagine the most typical case in which a gas enclosed in a piston is compressed, the force needed to do so has to counteract the pressure of the gas, and this pressure is due to the collision of the particles with the walls of the container, which is a random process that will differ from one realization to another. So, at each realization, we would need a different work. Of course, this difference will be very small in systems where the number of constituents is very large. However, there are systems where these statistical fluctuations are very important as mentioned in the introduction.

Consider that we can measure these discrepancies from one realization to another. Thus, if we repeat the same procedure we can construct a probability density $P(W)$. And we will be able to calculate some quantities like the average work, as shown below

$$\langle W \rangle = \int_{-\infty}^{\infty} W P(W) dW. \tag{1.4}$$

Or other statistical quantities such as variance.

Then, once this is understood, Jarzynski's equality expresses a relation between the mean value of a quantity that is a function of work and another quantity that is a function of the difference of free energies in the equilibrium states. Much more powerful than the inequalities provided by basic thermodynamics

$$\left\langle e^{-\beta W} \right\rangle = e^{-\Delta F}. \tag{1.5}$$

Where $\Delta F = F(T, \lambda_f) - F(T, \lambda_i)$ could be the equilibrium states shown in the figure 1.1. It is possible to see the clear connection made between work in processes arbitrarily far from equilibrium and quantities linked to equilibrium states. It seems quite similar to the result followed by the second principle (see equation 1.3). Hence, it can be proven that using Jensen's inequality $\left\langle e^{-\beta W} \right\rangle \geq e^{-\beta \langle W \rangle}$, combined with the equation 1.5 that we can obtain

$$\langle W \rangle \geq \Delta F. \tag{1.6}$$

For the first time, a generalization of the second law of thermodynamics appears for the average value of work. This is the lower bound mentioned in previous sections.

The most relevant implication of this result is precisely that the lower bound is for the average value of work but tells us nothing, strictly speaking, for the individual values of work at each realization. In other words, the consequence of this is that there are possibilities of obtaining values of work below the difference of free energies. What is a cycle like the one in figure 1.1 would imply obtaining work without altering the state of the system, in thermal equilibrium with only one source. A local violation of the second principle of thermodynamics would be obtained. Where this probability can be expressed as:

$$\text{Prob}(W < \Delta F) = \int_{-\infty}^{\Delta F} P(W) dW. \tag{1.7}$$

In the next chapter, we will proceed to show a proof of the theorem for a particular case in the scheme of two-time measurement protocol in quantum systems.

Chapter 2

Two-Time Measurement scheme (TTM) in non-equilibrium unitary dynamics

Resumen

En el presente capítulo se dará a conocer el marco de la medida de dos tiempos para sistemas unitarios y de no equilibrio; esto es, unitarios porque no hay procesos de disipación de energía, la entropía se mantiene constate, y de no equilibrios porque el sistema no transcurrirá, necesariamente, por procesos cuasiestáticos. Este esquema consiste en determinar el trabajo a partir de dos proyecciones de la energía al inicio y al final del protocolo. También se demostrará la igualdad de Jarzynski para el caso particular de un estado térmico de Gibbs al que se somete a un protocolo variando un parámetro de trabajo λ en el Hamiltoniano. Donde se verá, además, que todo este marco teórico no da cuenta del coste informacional de la medida ya que en la cota inferior que se establece para el valor medio trabajo no aparece reflejada ninguna magnitud asociada al hecho de medir. A parte de que en la segunda proyección de la energía se destruyen las coherencias, y estas poseen información de útilidad práctica.

From now on we will assume a very important simplification for the systems we are studying. We will assume no heat exchange with a thermal bath. Thus any given change in internal energy will be caused by work done by the environment. This situation is quite common in laboratory experiments, as stated in our reference literature [1]. This simplification will also allow us to use the Schrödinger equation to govern the dynamics of the system.

In this way, we will have statistics at two levels when measuring physical observables such as energy. One is due to thermal fluctuation due to coupling with the bath and the second is due to quantum fluctuations. Thus, quantum statistical mechanics already understands physical observables, including work, as random variables.

The two-measurement protocol consists of taking two projections of the energy, one at the beginning and the other at the end of the protocol. In this way, we will understand the work as the difference between these values. It corresponds to the most intuitive way of measuring

work.

Let us consider that we have an initial Hamiltonian $H(\lambda_i)$ whose eigenvectors are $|n\rangle$ with eigenvalues E_n^i. By taking a measure of the energy in the initial state we will have for each eigenvalue a probability $P_n = e^{-\beta E_n^i}/Z_i$ given by the diagonal matrix elements of the Gibbs matrix $\rho_i = \sum_n e^{-\beta\langle n|H(\lambda_i)|n\rangle}/Z_i \ |n\rangle\langle n|$. With $Z_i = \mathrm{tr}\{-\beta H(\lambda_i)\}$ the number of total states of the system-thermal bath system for a bath energy much larger than our system. This is no more than the partition function. β is equal to $1/k_bT$ where k_b is Boltzmann constant which it shall be considered as 1 and T is the temperature of the system.

Once we have collapsed the wave function to the state $|n\rangle$ and started to perform a certain protocol $\lambda(t)$ if we assume that the interaction with the thermal bath is very weak, this means that there is no heat exchange, so there is no dissipation during the execution of the protocol. Remember that it consists of, only, varying the working parameter. This implies that the entropy remains constant and it is the unitary operators that conserve this quantity (see annex A). Therefore, the evolution of the initial state in time $|\psi(t)\rangle$ will be given by the unitary time evolution operator or *driving* $U(t)$ of the following form:

$$|\psi(t)\rangle = U(t)|n\rangle. \tag{2.1}$$

After reaching a certain time $t = \tau$ we perform the second energy measurement. Where, in this case, we will have a Hamiltonian $H(\lambda_\tau)$ of eigenvalues E_m^f and eigenvectors $|m\rangle$. Therefore, the probability of obtaining a value of the energy E_m^f will be

$$|\langle m|U(\tau)|n\rangle|^2. \tag{2.2}$$

We conclude that for a value of the energy of E_n^i before performing the protocol and at the end of this E_m^f. The work will finally be the difference between these eigenvalues

$$W = E_m^f - E_n^i. \tag{2.3}$$

From all this reasoning we can draw two important conclusions:

- The first energy measurement is entirely due to thermal fluctuations since it starts from a Gibbs thermal state.
- While the second energy measurement is due to quantum fluctuations. That is, measurements are calculated on the evolved state by the Schrödinger equation.

Below is an outline showing the basic TTM procedure for the case discussed in this chapter. See figure 2.1.

2.1 Jarzynski equality proof within the TTM protocol

At this point, we can obtain the probability distributions for the work $P(W)$ and the characteristic function. Consider that the values E_n^i and E_m^f are obtained for the measurements of the energy, the initial and final state respectively. Well, because the result of the second

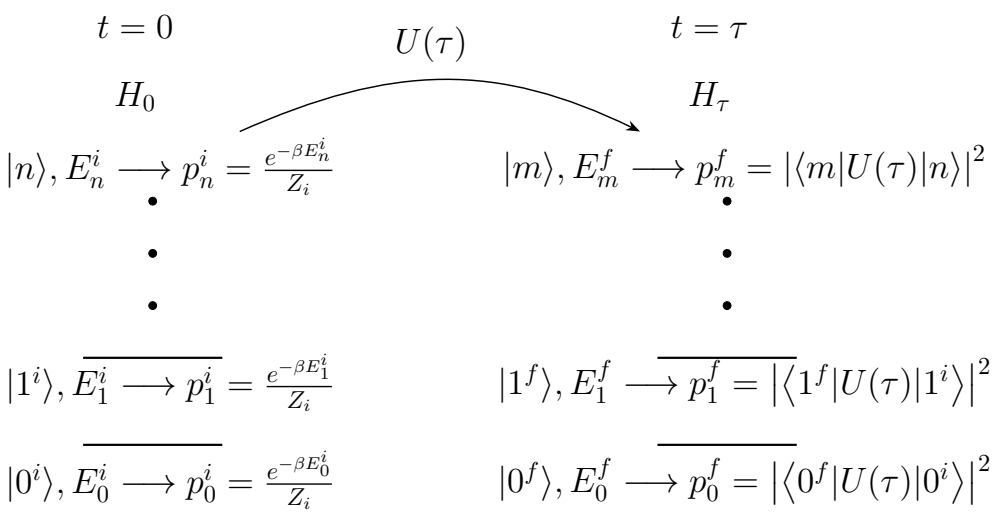


Figure 2.1: This figure represents the general scheme of the two-time measurement protocol (TTM) within this case. At the time $t = 0$ we have a Hamiltonian H_0, due to the contact with the thermal bath each eigenstate $|n\rangle$ of energy E_0^i will have a probability given by the corresponding diagonal element of the Gibbs operator, $p_n = \frac{e^{-\beta E_n^i}}{Z_i}$. While at time $t = \tau$ we will have a Hamiltonian H_τ of eigenstates $|m\rangle$ and energy E_m^f. Here, however, the probability is completely conditioned on the first measurement we obtain. If for the first measurement, the value E_n^i of energy is obtained, the wave function will have collapsed to the associated eigenstate $|n\rangle$. Then, once the protocol has started, the unitary time evolution operator will take the initial state to the final state $|\psi\rangle = U(\tau)|n\rangle$ therefore, the probability of obtaining a measure of E_m^f for the final energy will be the squared modulus of the amplitudes accompanying $|m\rangle$ in the evolved state $U(\tau)|n\rangle$.

measure, as mentioned at the beginning of this chapter, is strongly conditioned by the value of the first one. The probability of obtaining the value of E_m^f for the final state and E_n^i for the initial state is

$$P(E_m^f \cap E_n^i) = |\langle m|U(\tau)|n\rangle|^2 P_n, \tag{2.4}$$

where the elementary probability result for conditional variables has been recovered. That said if A_1 and A_2 were random variables, the probability of obtaining the intercept of both is

$$P(A_1 \cap A_2) = P(A_1|A_2)P(A_2). \tag{2.5}$$

Here, $P(A_i)$, $i = 1, 2$ represents the probability of the occurrence of the event A_1 or A_2. $P(A_1|A_2)$ expresses the conditional probability, i.e. the probability of the occurrence of A_1 having occurred A_2. In our case, P_n is the probability of the energy value of the thermal state, and $|\langle m|U(\tau)|n\rangle|^2$ is the probability calculated on the amplitudes of the evolved state. That is, the probability of obtaining an eigenstate $|m\rangle$ having obtained an initial state $|n\rangle$ which is $P(E_m^f|E_n^i)$.

Therefore, the probability of obtaining a work value W will be given by

$$P\left(W\right)=\sum_{m,n}\left|\left\langle m\right|U\left(t\right)\left|n\right\rangle\right|^{2}P_{n}\delta\left[W-\left(E_{m}^{f}-E_{n}^{i}\right)\right]. \tag{2.6}$$

Where $\delta[x]$ is the Dirac delta function. With this relation we sum the conditional probabilities of all possible cases and, thanks to the Dirac delta, we only take into account those whose difference in energy coincides with the value of the work.

Although this is an exact expression. Handling it directly would result in very complicated combinatorial formulae. This is why we will present the concept of characteristic function. That, in addition to providing operational simplicity, will be the bridge between the theory and the experimental proof of the fluctuation theorem. As we will see in the last chapters of this project with the quantum circuit. The *characteristic function* is defined, simply, as the Fourier transform of the probability distribution as follows

$$G\left(r\right)=\left\langle e^{irW}\right\rangle=\int_{-\infty}^{\infty}P\left(W\right)e^{irW}dW. \tag{2.7}$$

Thus, using the expression 2.6 we can calculate the characteristic function as follows

$$\begin{aligned}
G(r) &= \int_{-\infty}^{\infty} dW \left[\sum_{m,n} |\langle m|U(\tau)|n\rangle|^2 P_n \delta[W-(E_m^f-E_n^i)]\right] e^{irW} \\
&= \sum_{m,n} |\langle m|U(\tau)|n\rangle|^2 P_n e^{ir(E_m^f-E_n^i)} \\
&= \sum_{m,n} \langle n|U^\dagger(\tau)e^{irE_m^f}|m\rangle\langle m|U(\tau)e^{-irE_n^i}P_n|n\rangle \\
&= \sum_{m,n} \langle n|U^\dagger(\tau)e^{irH_f}|m\rangle\langle m|U(\tau)e^{-irH_i}\rho_{th}|n\rangle \\
&= \sum_{n} \langle n|U^\dagger(\tau)e^{irH_f}\underbrace{\sum_{m}|m\rangle\langle m|}_{\mathbb{1}}U(\tau)e^{-irH_i}\rho_{th}|n\rangle \\
&= \mathrm{Tr}\{U^\dagger(\tau)e^{irH_f}U(\tau)e^{-irH_i}\rho_{th}\}.
\end{aligned} \tag{2.8}$$

Where to go from the first to the second equality we have used the Dirac delta property $\int_{-\infty}^{\infty}dxf(x)\delta(x-a)=f(a)$. In the third and fourth equalities, we have conveniently accommodated these complex phases to change them for the associated operators, which, acting on their eigenstates, would return the constants back to us. In the fourth equality, the identity "$\mathbb{1}$" is recognized as the sum of the projectors over all the states. And, finally, we obtain an expression for the characteristic function set as a trace in Hilbert space.

This form of trace will be of great importance in the later chapters. For the moment, we can see that from this result we can extract the statistical moments of W by using the Taylor expansion of the exponential:

$$G\left(r\right)=\langle e^{irW}\rangle=1+ir\langle W\rangle-\frac{r^2}{2}\langle W^2\rangle-ir\frac{r^3}{3!}\langle W^3\rangle+... \tag{2.9}$$

From which we can extract a quantum expression for the mean value of work by making a Taylor's expansion of e^{irH_f} and e^{irH_i} in the expression 2.8 to give

$$\langle W\rangle=\langle H_f\rangle-\langle H_i\rangle. \tag{2.10}$$

See appendix B for more details. Hence, we say that the mean value of the work is nothing more than the difference between the mean values of the energy at the beginning and the end of the protocol. Which is very intuitive.

At this point, we can give r a value of $i\beta$ in the characteristic function (see equation 2.8) to prove Jarzynski's equality. As follows

$$\begin{aligned} G(r=i\beta)&=\mathrm{Tr}\left\{U^\dagger e^{\beta H_\tau}Ue^{\beta H_i}\frac{e^{-\beta H_i}}{Z_i}\right\}=\frac{1}{Z_i}\mathrm{Tr}\{U^\dagger e^{\beta H_\tau}U\}\\ &=\frac{1}{Z_i}\mathrm{Tr}\{e^{\beta H_\tau}\underbrace{UU^\dagger}_{\mathbb{1}}\}=\frac{Z_\tau}{Z_i}, \end{aligned} \tag{2.11}$$

where the explicit form of the density operator at the beginning of the protocol $\rho_{th}=\frac{e^{-\beta H_i}}{Z_i}$, the identity relation $e^{\beta H_i}e^{-\beta H_i}=\mathbb{1}$ and the cyclic property of the trace has been used.

Ending, as we know $Z=e^{\beta F}$. We can deduce

$$G(i\beta)=\langle e^{-\beta W}\rangle=e^{\Delta F}, \tag{2.12}$$

where we have recovered the general result presented in chapter 1. So again, if we use Jensen's inequality, we can easily arrive at the generalization of the second law for fluctuating systems $\langle W\rangle\geq\Delta F$.

By quick inspection, we see that we have a lower bound for the average work value that depends only on the free energy difference. However, we do not see any terms associated with the measuring process. Somehow this paradigm does not take into account the measurement as a thermodynamic process. Moreover, when projecting the energy, in the second measurement by changing from the evolved kets base to the eigenstate of the Hamiltonian at time τ, the coherences are destroyed. These coherences present information of practical use as in quantum computers [2]. In later chapters, we will see how the OTM scheme solves this inconsistency and turns out to be thermodynamically consistent.

Chapter 3

Application for magnetic resonance from the reference [1]

Resumen

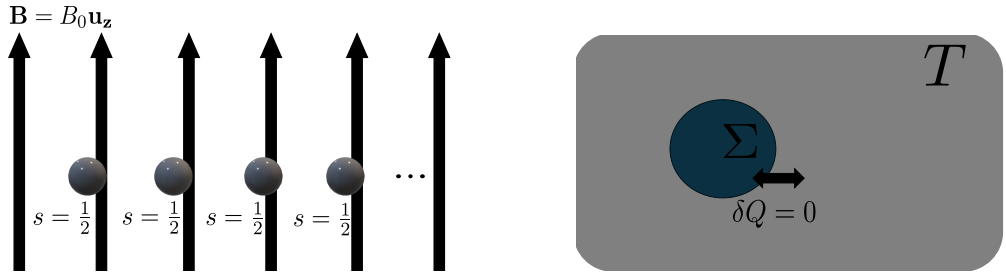
En este capítulo se aplicarán los conceptos de función característica y distribución de probabilidad del trabajo para el experimento de la resonancia magnética (N espines independientes sujetos a un campo magnético uniforme y una perturbación dependiente del tiempo perpendicular a este) bajo el paradigma del esquema de la medida de dos tiempos. Se hará uso de la interaction picture para resolver el problema monopartícula analíticamente, bajo una aproximación, quitándonos la dependencia temporal para comprobar los resultados que predice el teorema de las fluctuaciones para el valor medio del trabajo. Se verá, a partir del cálculo de la función distribución del trabajo, que se viola localmente el segundo principio de la termodinámica en una situación en la que se extrae trabajo de la transición spin antialineado-alineado al campo magnético sin alterar el estado del sistema. Se extrapolarán estos resultados para el caso de N partículas, y se verá como la probabilidad de que ocurran violaciones al segundo principio decae con e^N y, es este el motivo por lo que macroscópicamente no detectamos estas violaciones.

Following on from the literature review of [1]. The application of all these concepts, seen in the previous chapter, to the case of the magnetic resonance experiment, will be discussed. In addition to the physical implications of these concepts.

From now on, let us consider a system of N non-interacting particles of spin 1/2, which could be electrons, protons, neutrons, or any other fermionic particle, which we subject to a very strong magnetic field in the z-axis direction. All are weakly coupled to a thermal bath. As it is shown in the figure 3.1.

The total Hamiltonian will be the tensor product of the individual. That is, $\mathcal{H} = H_0^{(1)} \otimes H_0^{(2)} \otimes ... \otimes H_0^{(N)}$. Then the Hamiltonian of one particle will be the Hamiltonian of a particle with a magnetic moment of spin 1/2 interacting with a magnetic field $\mathbf{B}$. As follows

$$H_0 = -\boldsymbol{\mu_s}\mathbf{B} = -g_s\frac{\mu_B}{\hbar}\mathbf{S}\cdot\mathbf{B} = -g_s\frac{\mu_B}{\hbar}\frac{\hbar}{2}\sigma_z B_0, \tag{3.1}$$



(a) (b)

Figure 3.1: In the figure 3.1(a) we can see a very schematic representation of the problem of N non-interacting particles with equal spins 1/2 subjected to a magnetic field in the z-axis direction. Where the particles are represented by the black spheres and the magnetic field is given in the direction of the black arrows. While in the picture 3.1(b) we can see the schematic of the microcanonical collective, where the system Σ represents the system of non-interacting N spins weakly connected to a thermal bath, as we see in the figure, since $\delta Q = 0$; which fixes it at a temperature T.

where μ_s is the Bhor magnetron and g_s the Landau g-factor. If we measure the field in units of energy, where $\hbar = 1$ will be taken, the problem would be simplified to

$$H_0 = -\frac{B_0}{2}\sigma_z, \tag{3.2}$$

where B_0 corresponds to the characteristic precession frequency. As we see, we have a two-level Hamiltonian corresponding to spin-up and spin-down configurations of energies of $-\frac{B_0}{2}$ and $\frac{B_0}{2}$, respectively.

With all of this stated, the thermal density matrix will be given by

$$\rho_{th} = \begin{pmatrix} e^{B_0/2T}/Z & 0 \\ 0 & e^{-B_0/2T}/Z \end{pmatrix} = \begin{pmatrix} \frac{1}{2}(1+f) & 0 \\ 0 & \frac{1}{2}(1-f) \end{pmatrix}, \tag{3.3}$$

with f the equilibrium magnetization of the system, as we see $f = \langle\sigma_z\rangle_{th} = \tanh\frac{B_0}{2T}$ and Z the system partition function $Z = \mathrm{Tr}\{e^{-H_0/T}\} = 2\cosh B_0/2T$. Where we have used natural units, therefore, $k_b = 1$.

In our case, the protocol will consist of applying a time-dependent magnetic field contained in the xy plane of the form $\mathbf{B_1} = (B_1 \sin\omega t, B_1 \cos\omega t, 0)$. With B_1 several orders of magnitude below B_0 we will take the approximation $B_0 \gg B_1$. Thus the total Hamiltonian would be

$$H\,(t) = -\frac{B_0}{2}\sigma_z - \frac{B_1}{2}(\sigma_x \sin\omega t + \sigma_y \cos\omega t). \tag{3.4}$$

This field would play the role of perturbation. In which the time-dependent perturbation theory tells us that the probability of causing a transition from one state to another $|\pm\rangle$ will be maximal when the oscillation frequency ω of the field equals the natural oscillation frequency B_0. At this point, we will begin to solve the problem. That is, obtain the probability distribution function of the work as the difference of the mean values of the energy. All these

relations can be obtained from the time evolution operator $U(t)$. So, as is usual when working with time-dependent perturbations, we will move to the interaction picture where the problem, as we will see below, is simplified quite a lot.

We will work with the states $|\psi\rangle_I$, where the subscript I reflects that these are the kets of the interaction picture. And obey the following relation with the kets $|\psi\rangle_S$ where the subscript S indicates that these are the kets of the Schrödinger picture

$$|\psi\rangle_S = e^{i\omega\frac{\sigma_z t}{2}}|\psi\rangle_I. \tag{3.5}$$

It follows from this expression that the new time evolution operator $\tilde{U}(t)$ will be given by

$$U\left(t\right) = e^{i\omega t\frac{\sigma_z}{2}}\tilde{U}(t). \tag{3.6}$$

And, of course, it will follow the Schrödinger equation

$$i\partial_t\tilde{U} = \tilde{H}\tilde{U}. \tag{3.7}$$

Where $\tilde{H}$ takes the form

$$\tilde{H} = -\frac{(B_0-\omega)}{2}\sigma_z - \frac{B_1}{2}\sigma_y. \tag{3.8}$$

We can see this result in the annex C. Where a very useful relation has been used for a random matrix such that $\mathcal{M}^2 = \mathbb{1}$. Then, if α is an arbitrarily constant, the power series expansion of $e^{-i\alpha\mathcal{M}}$ leads directly to

$$\begin{aligned} e^{-i\alpha\mathcal{M}} &= 1 + \frac{(-i\alpha\mathcal{M})^2}{2!} + \frac{(-i\alpha\mathcal{M})^4}{4!} + \dots \\ &\quad + (-i\alpha\mathcal{M}) + \frac{(-i\alpha\mathcal{M})^3}{3!} + \frac{(-i\alpha\mathcal{M})^5}{5!} + \dots \\ &= 1 + \frac{-\alpha^2\cancel{\mathcal{M}^2}^{\mathbb{1}}}{2!} + \frac{\alpha^4\cancel{\mathcal{M}^4}^{\mathbb{1}}}{4!} + \dots \\ &\quad + (-i\alpha\mathcal{M}) + \frac{i\alpha^3\cancel{\mathcal{M}^2}^{\mathbb{1}}\mathcal{M}}{3!} + \dots \\ &= \mathbb{1}\cos\alpha - i\mathcal{M}\sin\alpha. \end{aligned} \tag{3.9}$$

As we can see there is no explicit dependence on time in 3.8. We can simply solve 3.7 to obtain:

$$U(t) = e^{i\omega t\sigma_z/2}e^{-i\tilde{H}t}. \tag{3.10}$$

We will again use the relation 3.9 to obtain an expression for 3.8. First we will rewrite the equation 3.8 as:

$$\tilde{H} = -\frac{\Omega}{2}\left(\sigma_z\cos\theta + \sigma_y\sin\theta\right), \tag{3.11}$$

where $\Omega = \sqrt{(B_0 - \omega)^2 + B_1^2}$, and $\tan\theta = \frac{B_1}{B_0 - \omega}$. Because $\sigma_i^2 = \mathbb{1}$ and $\sigma_i\sigma_j = i\epsilon_{ijk}\sigma_k \; \forall i, j \; / \; i \neq j$, where ϵ_{ijk} represents the antisymmetric tensor,it follows that $(\sigma_z \cos\theta + \sigma_y \sin\theta)^2 = \mathbb{1}$. Therefore, we can apply the equality 3.9. This leaves,

$$e^{-i\bar{H}t} = \mathbb{I}\cos\left(\frac{\Omega t}{2}\right) + i\left(\sigma_z\cos\theta + \sigma_y\sin\theta\right)\sin\left(\frac{\Omega t}{2}\right). \tag{3.12}$$

From where we can clearly identify $\mathcal{M}$ as $\sigma_z\cos\theta + \sigma_y\sin\theta$ and α as $-\frac{\Omega t}{2}$. Inserting this result into equation 3.10 finally yields an equality for the time evolution operator of the system

$$U(t) = \begin{pmatrix} u(t) & v(t) \\ -v^*(t) & u^*(t) \end{pmatrix}. \tag{3.13}$$

where,

$$\begin{aligned} u(t) &= e^{i\omega t/2}\left[\cos\left(\frac{\Omega t}{2}\right) + i\cos\theta\sin\left(\frac{\Omega t}{2}\right)\right], \\ v(t) &= e^{i\omega t/2}\sin\theta\sin\left(\frac{\Omega t}{2}\right) \end{aligned} \tag{3.14}$$

This would solve the mathematical problem. At this point, it is very important to analyze the physical meaning of the functions $u(t)$ and $v(t)$. For the moment, let's think about calculating the probability that starting from an initial state $|+\rangle$ we end up in a final state $|-\rangle$ at time t. This is the probability of anti-alignment with the magnetic field. This corresponds to a transition from a state with less energy to a more energetic state. That is, $|\langle -|U(t)|+\rangle|^2$. It is easy to see that this calculation corresponds to the modulus squared of the matrix element of the second row and first column of the time evolution operator, according to the usual convention for the basis of states space of spin $\{|+\rangle = (1,0), |-\rangle = (0,1)\}$. Hence corresponds to $|-v^*(t)|^2 = |v|^2$. So we can conclude that $|v|^2$ represents the probability of a jump occurring in the spin system. Moreover, thanks to the unitarity condition $UU^\dagger$ by introducing it in the following expression

$$\langle +|+\rangle = \langle +|U^\dagger U|+\rangle = |U|+\rangle|^2 = |u(t)|+\rangle - v^*(t)\,|-\rangle|^2 = |u|^2 + |v|^2 = 1. \tag{3.15}$$

We arrive at $|u|^2 + |v|^2 = 1$. So, $|u|^2$ means the probability that such a transition does not occur. Furthermore, we can see how in the equation 3.15 appears $v \propto \sin\theta$ so we can attribute to θ a meaning as the transition probability. Since $v(t)$ becomes maximal when $\sin\theta = 1$ and that happens when $\tan\theta = \frac{\pi}{2} \Leftrightarrow \omega = B_0$, see the definition for $\tan\theta$ to get the equation 3.11. The fact of $\omega = B_0$ is intuitive, what we are saying is that in a two-level quantum system, the transition probability is maximal when the frequency of the perturbation is the same as the frequency associated with the energy of separation of the levels. As if it absorbed a photon of just the right energy to jump levels. This is a consequence of the quantization of energy.

Once the time evolution operator is obtained, we can calculate the mean value of any physical observable. Uniquely using the relation $\langle A\rangle_t = Tr\left\{U^\dagger A U \rho_0\right\}$, where A is an observable.

One of particular interest is the magnetization in the z-direction of the system at time t. We will use it later when we obtain an expression for the probability distribution

$$\langle \sigma_z \rangle_t = f\left(1 - 2|v|^2\right) = f\left(\cos^2\theta + \sin^2\theta\cos\Omega t\right). \tag{3.16}$$

Where the fact that $|v|^2 + |u|^2 = 1$ and the definition of f in equation 3.3 have been used.

3.1 Average work and characteristic function

As we have seen so far, what we have is a two-level system in which the perturbation causes transitions to be made from one less energetic level to a more energetic level. Let us now think of the TTM protocol, and calculate the mean value of the work as the difference of the mean values of the unperturbed Hamiltonian at time 0 and at time t. Taking H_0 as representative only of the energy is justified since $H_0 \gg H_1$, where H_1 represents the Hamiltonian corresponding to the perturbation. Thus, the mean value of the energy at time 0 is

$$\langle H_0 \rangle_0 = -\frac{B_0}{2}\langle \sigma_z \rangle_0 = -\frac{B_0}{2} f. \tag{3.17}$$

From where the definition of f has been used as the magnetization of the system in the initial thermal state ρ_{th}. While for the mean value of H_0 after a time t we have the following

$$\langle H_0 \rangle_t = -\frac{B_0}{2}\langle \sigma_z \rangle_t = -\frac{B_0}{2} f(1 - 2|v|^2), \tag{3.18}$$

where we recover what we have seen previously for the magnetization at the end of the protocol, see equation 3.16. Taking the difference between the two we obtain the average value of the work

$$\langle W \rangle_t = f B_0 |v|^2 = f B_0 \frac{B_1^2}{\Omega^2}\sin^2\left(\frac{\Omega t}{2}\right). \tag{3.19}$$

Our final result tells us that the average value of work oscillates with a frequency $\Omega/2$ whose maximum is $f B_0 \frac{B_1^2}{\Omega^2}$ and would be reached at times $\frac{\pi}{\Omega}p$, with p and odd integer. It is observed that the maximum value of work is proportional to fB_0, the magnetization of the system and the characteristic frequency, multiplied by a Lorentzian function since $\Omega = B_1^2/((B_0^2 - \omega)^2 + B_1^2)$, this function becomes maximum at the resonance condition ($\omega = B_0$) giving a value for the work of fB_0. Because the evolution of the system is governed by a unitary operator we arrive at a periodic expression for the work. This is because, as mentioned above, there is no dissipation. Once a period of the perturbation has elapsed we recover the same system, so it makes sense that the mean values of physical quantities follow a symmetric behavior concerning time translations.

Another result we see as a consequence of the second law for fluctuating systems is that as the free energy is time-independent, since $B_0 \gg B_1$, $F(T, Z) = T\ln(Z)$, this implies $\Delta F = 0$, so from equation 1.6 we finally have $\langle W \rangle \geq 0$. And we see this perfectly in the expression 3.19.

Let us go one step further. Consider obtaining the probability distribution function of the work using the characteristic function. Thus, applying the relation 2.8 we arrive at by simple matrix multiplication

$$G(r) = |u(t)|^2 + |v(t)|^2 \left\{ \frac{(1+f)}{2} e^{iB_0 r} + \frac{(1-f)}{2} e^{-iB_0 r} \right\}. \tag{3.20}$$

Bearing in mind that we have to use H_0 as H_0 and H_τ in the trace. Then, from this simple expression, we can obtain the probability function from the inverse Fourier transform. That is to say,

$$P(W) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dr G(r) e^{-iWr}. \tag{3.21}$$

If we do this we arrive at

$$P(W) = |u|^2 \delta(W) + |v|^2 \frac{1+f}{2} \delta\left(W - B_0\right) + |v|^2 \frac{1-f}{2} \delta\left(W + B_0\right). \tag{3.22}$$

Let us carefully analyze this result to delve deeper into the physical meaning. First, we see that it is only possible to obtain 3 values for the work, i.e. $W = \{0, +B_0, -B_0\}$, because of the definition of the Dirac delta. This corresponds to the three possible cases in a two-level system, see figure 3.2, i.e. we have the possibility that the spin value is not modified in any case no work is done ($P(W = 0)$). The next case is that there is a transition from the aligned to the anti-aligned spin state where the work would be positive since the first is less energetic than the second $P(W = +B_0)$. And the last one, from anti-aligned to aligned where the system would produce work on the surroundings $P(W = -B_0)$ since it is jumping from a more energetic level to a less energetic level.

However, the equation 3.22 is quite intuitive and can be derived heuristically. Consider the case of an up-down flip where the value of work is $+B_0$. The probability of this happening is the probability of, first, obtaining the state $|+\rangle$ in the thermal state, i.e. $\langle +|\rho|+\rangle = (1+f)/2$, and, second, the conditional probability of obtaining the anti-aligned state starting from the aligned state, i.e. $|\langle -|U|+\rangle|^2$, which we saw in the previous section, corresponds to the probability of a transition occurring, $|v|^2$. As we can see, the term accompanying the delta $\delta\left(W - B_0\right)$ is recovered. Repeating this reasoning for the other two cases we can arrive at the equation above.

If we look carefully we see that there is a non-zero probability that the system produces work to the surroundings, for a case of a down-up flip in spin. This corresponds to a local violation of the second principle. The violation occurs with a probability $P(W = -B_0) = |v|^2(1-f)/2$, beware that it will always be smaller than the probability that it does not occur since $(1-f)/2 \leq (1+f)/2$. This makes the final result $\langle W \rangle \geq 0$ (see equation 3.19) which indicates that the violation is the exception never the rule.

Thus we have seen how for the case of a single particle a case appears which locally violates the second principle. If one wishes to check these probabilities experimentally in the laboratory, it is interesting to express all these probabilities using the magnetization in the initial state f and at time t, as shown in equation 3.16. Therefore, a couple of manipulations of equation 2.4 using the definition of magnetization in time t yields the following:

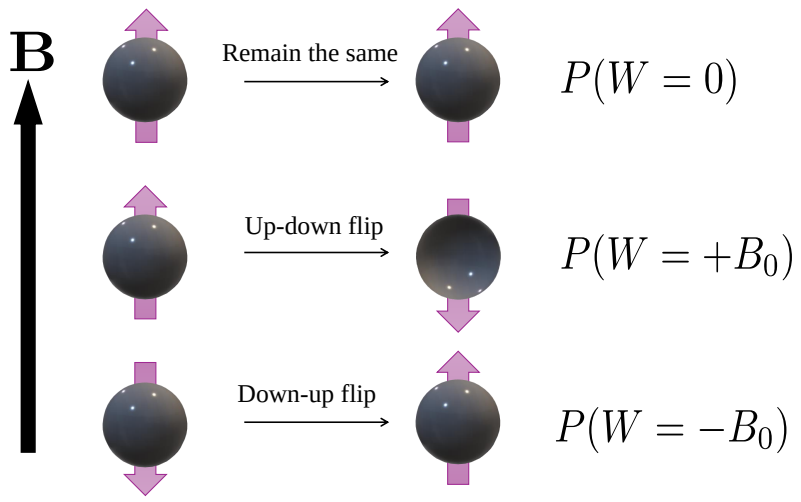


Figure 3.2: In this schematic representation we can see the three possible situations in a two-level quantum system. To the left of the diagram, the magnetic field along the z-axis is represented by a black arrow. Then we can see the particles and their spin z-component value represented with black spheres and purple arrows respectively.

$$\text{Prob}\left(W=\pm B_0\right)=\left(\frac{f-\langle\sigma_z\rangle_t}{2f}\right)\frac{1\pm f}{2}. \tag{3.23}$$

The significance of this expression is that magnetization is a macroscopic observable that can be measured in a laboratory.

3.2 Work measurements for a large number of particles.

The above results express the work done by a magnetic field on a particle of spin 1/2. Although this is an exact result and can be experimentally verified. The most usual is not to have a single particle but a system of many particles. So suppose we have N particles of spin 1/2 that do not interact with each other otherwise the problem would become quite difficult, one would have to consider, for example, solving the problem using a DFT (Density Functional Theory) model. In this way the total work $\mathcal{K}$ done by the N particles corresponds to the sum of the individual works

$$\mathcal{W}=W_1+W_3+...+W_N. \tag{3.24}$$

The different values of work $\{W_i\}_{i=1}^N$ can be treated as identically distributed independent variables. Therefore, statistical parameters such as the mean of the total work can be put as the sum of the mean values in this way. And, these, in turn, are all equal, thus, $\langle\mathcal{W}\rangle=N\langle W\rangle$. Then, many quantities like the characteristic function take a very simple form, that is

$$\mathcal{G}(r)=\left\langle e^{ir\mathcal{W}}\right\rangle=\left\langle e^{irW_1}\right\rangle\cdot\left\langle e^{irW_2}\right\rangle\cdot...\cdot\left\langle e^{irW_N}\right\rangle=\left\langle e^{irW}\right\rangle^N=G(r)^N. \tag{3.25}$$

Where in the third equality the fact that all spins are equal has been used. So if we look closely at the equation we can see that what we are saying is that the characteristic function of a system of non-interacting particles is the product of their individuals characteristic functions.

Then, the next step would be to obtain the probability distribution function for the system of particles, in the same way as we did for the case of 1 particle; by taking the inverse Fourier transform, as indicated in the expression 3.21. But first, as indicated in our reference literature [1], we will introduce the following changes in the notation, which will help us to deepen our understanding of the physical meaning of the characteristic function. We will take $b_0 = |u|^2$ and $b_\pm = |v|^2(1 \pm f)/2$. Implementing this in equation 3.25, the equation would read as follows

$$\mathcal{G}(r) = (b_0 + b_+ e^{iB_0 r} + b_- e^{-iB_0 r})^N. \tag{3.26}$$

If we develop the product, when we combine them, we get all the terms from $(e^{iB_0 r})^{-N}$ to $(e^{iB_0 r})^N$, so that it can be read as

$$\mathcal{G}(r) = \sum_{k=-N}^{N} \Gamma_k e^{iB_0 r k}. \tag{3.27}$$

Where the coefficients Γ_k are combinatorial combinations of the b_0, b_+ and b_-, the algebraic development can be found in annex C. Then, applying the inverse of the Fourier transform to obtain the work distribution function

$$\begin{aligned} P(\mathcal{W}) =& \frac{1}{2\pi} \int_{-\infty}^{+\infty} dr G(r) e^{-ir\mathcal{W}} = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dr \left[\sum_{k=-N}^{N} \Gamma_k e^{irB_0 k} \right] e^{-ir\mathcal{W}} \\ &= \sum_{k=-N}^{N} \Gamma_k \underbrace{\left(\frac{1}{2\pi}\right) \int_{-\infty}^{+\infty} dr e^{-i(\mathcal{W} - B_0 k)r}}_{\delta(W - B_0 k)} = \sum_{k=-N}^{N} \Gamma_k \delta(\mathcal{W} - B_0 k). \end{aligned} \tag{3.28}$$

We finally arrived at the desired result. As can be seen, a similar result to the single-particle case is obtained in equation 3.22. This expression tells us that we can have the $2N+1$ values for the work that sweeps all the possibilities from all the spins becoming anti-aligned with the magnetic field, in which case $\mathcal{W} = NB_0$ and the case of all of them becoming aligned, $\mathcal{W} = -NB_0$.

This form for the distribution of work is a consequence of the form of the characteristic function in 3.25. It can be interpreted as an N-step random walk with three possible steps, i.e., we can take the step e^{irB_0}, with a probability of b_+, we can also move towards e^{-irB_0} with the respective probability b_-, or, simply not move at all, whose probability is b_0. Then the N appearing in the exponent of the equation 3.25 expresses the result of having taken N steps.

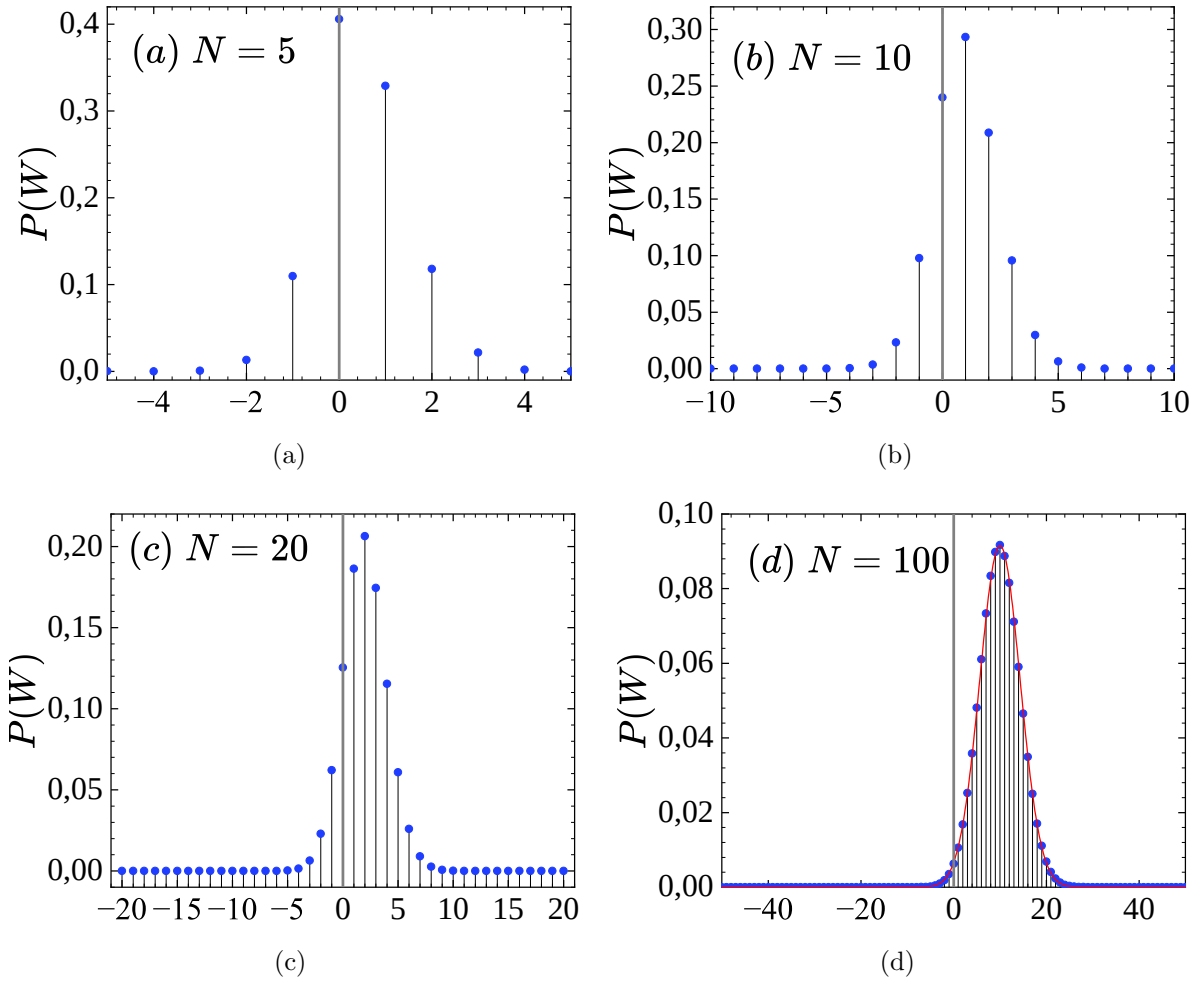


Figure 3.3: The probabilities of the different values of the work of the whole system of the N non-interacting spins are plotted. Where the values of $B_0 = 1$, $\omega = 0.8$, $B_1 = 0.1$, $f = 0.5$ and $t = \frac{\pi}{\Omega}$ have been assigned. For 4 different cases of $N = 5, 10, 20$ and 100 in figures 3.3(a), 3.3(b), 3.3(c) and 3.3(d) respectively. Here, in addition, the Gaussian of the same mean and variance of the spin system has been plotted with a red line in figure 3.3(d). This figure is adapted from our main reference [1].

As a result, we can easily represent the probability distribution given in the equation 3.28. This is shown in the figure 3.3. Recalling a bit, our system is the one in figure 3.1(b) with the Σ system corresponds with the non-interacting N spin particles to which we have plugged a perturbation, where the effect is to interact with the magnetic momentum of the particle and cause transitions between the aligned and anti-aligned states with the magnetic field in the z-axes. With probabilities given by the squared modulus of certain matrix elements of the time evolution operator as mentioned before. Well, in the figures we see how the perturbation is able to cause transitions between higher and lower energy states resulting in negative work values. This results in local violations of the second principle. Corresponding to the values to the left of the grey line. What we see is a situation where the initial thermal state favors an anti-alignment with the magnetic field and the perturbation is able to cause the transition to

the aligned state resulting in work being done without altering the state of the system since $B_0 \gg B_1$.

One thing that catches our attention is that as we increase the number of constituents the probability of violations of the second principle decreases. And, this probability, as our reference indicates, goes with decreasing exponential. This is precisely why we do not detect violations of the second principle at the macroscopic scale. To conclude the discussion of these results, a Gaussian distribution with the same mean and variance as the distribution of the particle system is drawn in the figure 3.3(d). This is to keep in mind the central limit theorem, which tells us that the distribution function of a sum of independent random variables is the convolution product of the independent distributions and that in the limit where the number of variables becomes infinite, this distribution is a Gaussian one.

Chapter 4

One Time Measurement scheme (OTM) and fluctuation theorem with experimental verification (Summary of [2, 3])

Resumen

En el presente capítulo se ha introducido el teorema de las fluctuaciones bajo el esquema de la medida única (OTM), obteniendo una igualdad de Jarzynsky modificada que da cuenta del coste informacional de la medida y soluciona el paradigma termodinámico de la TTM que no da cuenta de este coste. La igualdad de Jarzynsky da lugar a una generalización del segundo principio con una cota inferior mejor establecida que para el caso de la TTM, donde sí que se incorpora la media como parte del proceso termodinámico. El trabajo, visto desde el esquema OTM consiste en una primera medida de la energía inicial donde se proyecta sobre los autoestados del Hamiltoniano inicial y una segunda donde lo que se mide es un Hamiltoniano condicional que está definido tal que los vectores evolucionados son estados puntuales de este, por lo que en esa segunda no se destruyen coherencias, ni se pierde la información portada por los vectores evolucionados. Se ha hecho hincapié en que el esquema OTM es un esquema TTM no destructivo debido a que en esa segunda medida no se destruyen los estados evolucionados. Y, a partir de la expresión para las funciones características, se ha podido ver que las rotaciones que actúan sobre los estados térmicos pueden ser recreadas en un ordenador cuántico. Lo que plantea una prueba experimental para el teorema. Se ha trabajado a fondo en la conexión entre como puede ser obtenida la función característica y las operaciones necesarias en un ordenador cuántico para acceder a esta cantidad, desarrollando el álgebra que hay detrás y proveyendo de una explicación a los resultado obtenidos por nuestra referencia para la OTM [2].

So far we have developed an entire framework around the TTM scheme. And we have proved Jarzynsky's equality for a particular case as in chapter 2. So, the next step will be to present a different scheme for measuring work. The OTM (one-time measurement) scheme. This scheme has the power that it will preserve the quantum coherences and correlations, very

importantly, it will solve the thermodynamic inconsistency of the previous paradigm since it will take into account the informational cost of the measurement [2].

The OTM scheme consists of a TTM scheme in which the second energy measure is replaced by a measurement of a conditional Hamiltonian in which the information provided in the basis of the evolved kets $U|n\rangle$ is not destroyed by being projected into the eigenstates basis of the final state Hamiltonian. In this way, we will be able to show that Jarzynsky's equality will include an extra term related to the relative quantum entropy difference between the conditional thermal state and the Gibbs thermal state corresponding to the final Hamiltonian.

So, let us return to our closed quantum system described by a thermal Gibbs state of the form $\rho_0^{eq} = \exp\{\beta \mathrm{H}_0\}/Z_0$ where Z_0 is the partition function and H_0 is the initial Hamiltonian. As we already know from chapter 2 and completed in annex A, the evolution of the states will be given by a unitary evolution operator U. According to the OTM, if we make a first measurement of the energy, we define the work as the difference of the corresponding mean value in the evolved state and this first initial measurement, as follows

$$\widetilde{W}(0^+, E_n) = \langle H_\tau \rangle_\tau - E_n. \tag{4.1}$$

This quantity is also called *conditional work* since it depends exclusively on the initial measure of energy. Proceeding as in the case of the TTM scheme, the forward conditional work distribution will be given by

$$\widetilde{P}_f(W) = \sum_{n=1}^{d} \frac{e^{-\beta E_n}}{Z_0} \delta\left(W - \widetilde{W}_n\right), \tag{4.2}$$

with this relation, we express that the probability of obtaining a work value of $W(0^+, E_n)$ is simply the probability of obtaining the state $|n\rangle$ in the initial thermal state. So if we calculate the mean value of $\left\langle e^{-\beta W} \right\rangle_{\widetilde{P}_f}$ we obtain Jarzynsky's equality for the OTM equation as follows

$$\begin{aligned} \left\langle e^{-\beta W} \right\rangle_{\widetilde{P}} &= \int dW e^{-\beta W} \widetilde{P}_f(W) = \sum_{n=1}^{d} \int dW e^{-\beta W} \frac{e^{-\beta E n}}{Z_0} \delta\left(W - \widetilde{W}_n\right) \\ &= \sum_{n=1}^{n} e^{\beta(<n|U^\dagger H_\tau U|n\rangle - E n)} \frac{e^{-\beta E_n}}{Z_0} = \frac{\sum_{n=1}^{n} e^{-\beta \left\langle n|U^\dagger H_\tau U|n\right\rangle}}{Z_0} \cancel{e^{\beta E_n} \cdot e^{-\beta E_n}} 1 = \frac{\widetilde{Z}_\tau}{Z_0}. \end{aligned} \tag{4.3}$$

Where we have defined $\widetilde{Z}_\tau = \sum_{n=i}^{N} e^{-\beta \left\langle n|U^\dagger H_\tau U|n\right\rangle}$ as the conditional partition function, which is the normalization factor of the conditional thermal state $\widetilde{\rho}_\tau = \sum_{n=i}^{d} e^{\left\langle n|U^\dagger H_\tau U|n\right\rangle}/\widetilde{Z}_\tau U |n\rangle\langle n| U^\dagger$. Where if we use the definition of quantum relative entropy between the final Gibbs equilibrium state and the final conditional state

$$S\left(\widetilde{\rho}_\tau \| \rho_\tau^{\mathrm{eq}}\right) = \mathrm{Tr}\left\{\widetilde{\rho}_\tau \ln \widetilde{\rho}_\tau\right\} - \mathrm{Tr}\left\{\widetilde{\rho}_\tau \ln \rho_\tau^{\mathrm{eq}}\right\}. \tag{4.4}$$

Where the first term is called the negentropy of the conditional thermal state $\widetilde{\rho}_\tau$ and is calculated as follows

$$\begin{aligned}\mathrm{Tr}\left\{\widetilde{\rho}_\tau \ln(\widetilde{\rho}_\tau)\right\} &= \mathrm{Tr}\left\{\widetilde{\rho}_\tau\left[\ln(\sum_{n=1}^{d} e^{-\beta\langle n|U^\dagger H_\tau U|n\rangle}U|n\rangle\langle n|U^\dagger - \ln(\widetilde{Z}_\tau)\right]\right\}\\ &= -\beta\mathrm{Tr}\{\widetilde{\rho}_\tau\sum_{n=1}^{d}\langle n|U^\dagger H_\tau U|n\rangle\, U|n\rangle\langle n|U^\dagger\} - \mathrm{Tr}\{\widetilde{\rho}_\tau\ln(\widetilde{Z}_\tau)\}\\ &= -\ln(\widetilde{Z}_\tau) - \beta\frac{1}{\widetilde{Z}_\tau}\sum_{n=1}^{N} e^{-\beta\langle n|U^\dagger H_\tau U|n\rangle}\langle n|U^\dagger H_\tau U|n\rangle\\ &= -\ln\{\widetilde{Z}_\tau\} - \beta\langle H_\tau\rangle_\tau,\end{aligned} \tag{4.5}$$

while the second term is the cross entropy of both states. Similarly, its final expression is

$$\begin{aligned}\mathrm{Tr}\left\{\tilde{\rho}_\tau \ln\left(\rho_\tau^{\mathrm{eq}}\right)\right\} &= \mathrm{Tr}\left\{\widetilde{\rho}_\tau\left[\ln(e^{-\beta H_\tau} - \ln(Z_\tau)\right]\right\}\\ &= -\beta\mathrm{Tr}\{\widetilde{\rho}_\tau H_\tau\} - \mathrm{Tr}\{\widetilde{\rho}_\tau\ln(Z_\tau)\}\\ &= -\ln(Z_\tau) - \beta\frac{1}{\widetilde{Z}_\tau}\mathrm{Tr}\left\{\sum_{n=1}^{d} e^{-\beta\langle n|U^\dagger H_\tau U|n\rangle}U|n\rangle\langle n|U^\dagger H_\tau\right\}\\ &= -\ln\{Z_\tau\} - \beta\frac{1}{\widetilde{Z}_\tau}\sum_{n,n'} e^{-\beta\langle n|U^\dagger H_\tau U|n\rangle}\underbrace{\langle n'|U^\dagger U|n\rangle}_{\delta(n-n')}\langle n|U^\dagger H_\tau U|n'\rangle\\ &= -\ln\{Z_\tau\} - \beta\langle H_\tau\rangle_\tau.\end{aligned} \tag{4.6}$$

Therefore, we can express $e^{-S(\widetilde{\rho}_\tau||\widetilde{\rho}_\tau^{eq})} = \widetilde{Z}_\tau/Z_\tau$ so by adding this definition to equation 4.3 we can conclude that

$$\left\langle e^{-\beta W}\right\rangle_{\tilde{\mathcal{P}}} = e^{-\beta\Delta F}e^{-S\left(\tilde{\rho}_\tau\|\rho_\tau^{eq}\right)}, \tag{4.7}$$

where $\Delta F = -1/\beta\ln(Z_\tau/Z_0)$. So we arrive at Jarzynsky's modified equality. If we compare it with the relation 1.5 we see that a term appears that tells how different the Gibbs thermal states and the conditional thermal state are. If we use Jensen's equality:

$$\beta\langle W\rangle_{\tilde{P}} \geq \beta\Delta F + S\left(\tilde{\rho}_\tau\|\rho_\tau^{\mathrm{eq}}\right). \tag{4.8}$$

We obtain a new version of the relation 1.6, i.e. of the second law for fluctuating theorems. This time there is a lower bound which gives us more information than if we only include the difference of free energies of the thermal states. We are accounting for the informational cost of measuring, with the form 4.7 we include the changes in the thermodynamic state introduced by measuring. The lower bound turns out to be more significant, in one of our reference works, [3], it shows how for the case of the parametric harmonic oscillator this result can provide much more information on how much work is available in the system.

4.1 Equivalence between OTM and TTM schemes

Let's think from the TTM point of view but defining a new physical quantity described by

$$G_\tau \equiv \sum_{n=1}^{d} \langle n \left| U^\dagger H_\tau U \right| n \rangle \, U \left| n \right\rangle \langle n | \, U^\dagger. \tag{4.9}$$

Where the $|n\rangle$ corresponds to the eigenstates of the initial Hamiltonian. At time $t = 0$ of starting the protocol we measure over the eigenenergies of H_0 so we will obtain a state $|n\rangle$. When performing the protocol we will have an evolved state $U|n\rangle$. Subsequently, at time $t = \tau$ if we measure the observable G_τ on the basis of evolved kets we will obtain precisely the eigenvalue $\langle n|U^\dagger H_\tau U|n\rangle$. The information carried by $U|n\rangle$ will not be destroyed since the evolved kets are *pointer state* of G_τ [12].

Thus we can define work as the difference in energies between the mean value of the energy in the final state and the energy in the initial state. If we express its probability distribution function, it would take the form

$$\widetilde{P}_f(W) = \sum_{i=1}^{d} \frac{e^{-\beta \langle n|H_0|n\rangle}}{Z_0} \underbrace{\left| \langle n \left| U^\dagger U \right| n \rangle \right|^2}_{\mathbb{1}} \delta\left(W - \widetilde{W}_i\right). \tag{4.10}$$

Here we express, as in chapter 2, the conditional probability that once one state is obtained in the thermal bath, the state $U|n\rangle$ is obtained whose associated eigenvalue corresponds to $\langle n|U^\dagger H_\tau U|n\rangle$ and we see that this expression is precisely the same as 4.2.

So we see that the OTM scheme is really a non-destructive TTM scheme. Since in that second measurement, the information carried by $U|n\rangle$ is preserved.

4.2 Experimental verification of the fluctuation theorem on a quantum computer

From now on we will use the concept of the backward distribution function to demonstrate a symmetry that exists with the forward distribution function that can be tested on a quantum computer, and hence we will have an experimental proof of the fluctuation theorem.

To get the backward distribution function, we now start from the state $U|n\rangle$, and evolve the system backward in time with $U^\dagger$ in such a way that the final states $U^\dagger U|n\rangle = |n\rangle$ are point states of H_0, so that a measurement of the initial energy will not destroy the information carried by the state $|n\rangle$. So we can deduce:

$$\widetilde{P}_b(-W) \equiv \sum_{i=1}^{d} \frac{e^{-\beta \langle n \left| U^\dagger H_\tau U \right| n \rangle}}{\widetilde{Z}_\tau} \delta\left(-W + \widetilde{W}_i\right). \tag{4.11}$$

Where in this case we see that it is the energy of the initial state that is completely dependent on the final state. And the minus in the argument of the function reminds us that now time goes backwards, so if we ask ourselves what is the probability of obtaining work $W > 0$, from the point of view of the backward process, we are asking the probability that the system does work on the surroundings.

Applying the relation 2.8 to express the characteristic function as the trace of operators, it follows that

$$\begin{aligned}\widetilde{C}_f(u) &= \mathrm{tr}\left\{U^\dagger e^{iuG_\tau} U e^{-iuH_0}\rho_0^{\mathrm{eq}}\right\}\\ \widetilde{C}_b(u) &= \mathrm{tr}\left\{U e^{iuH_0}U^\dagger e^{-iuG_\tau}\widetilde{\rho}_\tau\right\}.\end{aligned} \tag{4.12}$$

And, here comes one of the main results of our reference bibliographies [2]. You can arrive at the fluctuation theorem and the following symmetry relation just by taking

$$\begin{aligned}\frac{\widetilde{C}_f(u)}{\widetilde{C}_b(-u+i\beta)} &= \frac{\mathrm{tr}\left\{U^\dagger e^{iuG_\tau}Ue^{-iuH_0}\rho_0^{\mathrm{eq}}\right\}}{\mathrm{tr}\left\{Ue^{i(-u+i\beta)H_0}U^\dagger e^{-i(-u+i\beta)G_\tau}\widetilde{\rho}_\tau\right\}}\\ &= \frac{\widetilde{Z}_\tau}{Z_0}\frac{\mathrm{tr}\left\{U^\dagger e^{iuG_\tau}Ue^{-iuH_0}e^{-\beta H_0}\right\}}{\mathrm{tr}\left\{Ue^{i(-u+i\beta)H_0}U^\dagger e^{-i(-u+i\beta)G_\tau}e^{-\beta G_\tau}\right\}}\\ &= \frac{\widetilde{Z}_\tau}{Z_0}\frac{\mathrm{tr}\left\{U^\dagger e^{iuG_\tau}Ue^{-iuH_0}e^{-\beta H_0}\right\}}{\mathrm{tr}\{U^\dagger e^{iuG_\tau}\underbrace{e^{\beta G_\tau}e^{-\beta G_\tau}}_{\mathbb{1}}Ue^{-iuH_0}e^{-\beta H_0}\}} = e^{-\beta\Delta F - S\left(\widetilde{\rho}_\tau\|\rho_\tau^{\mathrm{eq}}\right)}.\end{aligned} \tag{4.13}$$

This symmetry relation can be verified on a quantum computer because they are able to obtain the characteristic functions. If we look carefully at how the forward characteristic function is constructed. We realize that what we have is a thermal state ρ_0^{eq} to which a series of rotations are made, rotations, since all the matrices involved are unitary. Which is precisely what quantum computers do. They start from a series of states, 'qubits', and perform unitary operations on them, called 'gates'. Thus a quantum circuit, taken from our reference [2], to compute the forward characteristic function would be like in the figure 4.1.

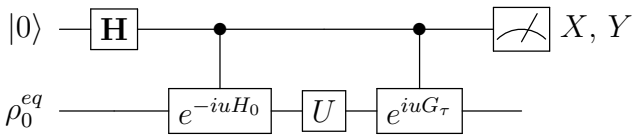


Figure 4.1: Quantum circuit with an ancilla qubit prepared in a state $|0\rangle$. This is an auxiliary state that will help us to measure. And, a thermal state ρ_0^{eq}, also called target state, on which the different rotations will act. In this circuit, the following act on the ancilla: a Hadamart gate, denoted by $\mathbf{H} = \frac{1}{\sqrt{2}}\begin{pmatrix}1 & 1\\ 1 & -1\end{pmatrix}$, and two control gates, denoted by black dots, whose function is to apply the rotation that appears in the black square in the target state only if the ancilla turns out to be $|1\rangle$, in the case that it is $|0\rangle$ it will not be applied. And in the bottom line, we have only the rotations that will act on the target state. And, at the end of the line above it is represented the measure of the X and Y Pauli matrices. Due to the following relation $\langle X\rangle = \mathrm{Re}\{\widetilde{C}_f(u)\}$ and $\langle Y\rangle = \mathrm{Im}\{\widetilde{C}_f(u)\}$ are precisely given. This circuit was taken from the reference [2].

Note that as in the expression 4.12 for the forward characteristic function in the circuit of figure 4.1 we are applying all rotations. For example, we have that, on the thermal state

will act the rotation associated with H_0, then the driving, and finally, the rotation associated with G_τ.

As mentioned in the introduction, the characteristic function is very relevant as it provides the bridge to an experimental proof of the fluctuation theorem in a quantum machine. And the connection lies precisely in the fact that, if we have a unitary operator V and we want to calculate its average value in a given thermal state ρ, that is, we want to know the trace of this operator times one state or, in other words, $\mathrm{Tr}\{V\rho\}$. It suffices to measure the mean values of the Pauli matrices $X \otimes \mathbb{1}$ and $Y \otimes \mathbb{1}$ in the total space formed by the tensor product of the states of the qubit ancilla and the thermal state. Since we can calculate the real and imaginary part of the c-number $\widetilde{C}_f(u)$ as their mean values .

Let us demonstrate this for a thermal state $\rho^{eq} = \begin{pmatrix} p_0 & 0 \\ 0 & p_1 \end{pmatrix}$ with $p_0, p_1 \in \mathbb{R}$ and a rotation $V = \begin{pmatrix} v_{00} & v_{01} \\ v_{10} & v_{11} \end{pmatrix}$ which would represent the application of all the previous rotations for calculating the characteristic function. If we calculate the mean value of the operator V for this state, note that V does not need to be an observable, we obtain $\mathrm{Tr}\{V\rho^{eq}\} = p_0 v_{00} + p_1 v_{11}$. Let us now access this quantity from the quantum circuit shown in figure 4.1 .

First of all let us consider the action of the Hadamard gate on the ancilla $|0\rangle = (1,0)^T$ in the basis $\{|0\rangle, |1\rangle\}$ in the following way

$$\mathrm{H}|0\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle). \tag{4.14}$$

We see that we obtain the state $|+\rangle$, one eigenstate of X. The Hadamard gate is a basic gate in quantum computing that manages to generate precisely the superposition of states that is so necessary for quantum computing. It is this superposition that makes quantum computation different from classical.

From now on the state of the total system will be the tensor product of the superposed state and the thermal state as follows

$$\begin{aligned} \rho_0 \otimes \rho^{eq} &= |+\rangle\langle+| \otimes (p_0 |0\rangle \langle 0| + p_1 |1\rangle \langle 1|) \\ &= \frac{1}{2} p_0 |0,0\rangle \langle 0,0| + \frac{1}{2} p_0 |1,0\rangle \langle 0,0| + \frac{1}{2} p_1 |0,1\rangle \langle 0,1| \\ &+ \frac{1}{2} p_1 |1,1\rangle \langle 0,1| + \frac{1}{2} p_0 |0,0\rangle \langle 1,0| + \frac{1}{2} p_0 |1,0\rangle \langle 1,0| \\ &+ \frac{1}{2} p_1 |0,1\rangle \langle 1,1| + \frac{1}{2} p_1 |1,1\rangle \langle 1,1| . \end{aligned} \tag{4.15}$$

We will now apply the unitary transformation imposed by V to the total state. In other words, we will evolve the state according to the quantum circuit. To do so, let us consider the following matrix expressions in the full space

$$V = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & u_{00} & u_{01} \\ 0 & 0 & u_{10} & u_{11} \end{pmatrix}, \; V^\dagger = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & u_{00}^* & u_{10}^* \\ 0 & 0 & u_{01}^* & u_{11}^* \end{pmatrix} \tag{4.16}$$
with base: $\{|00\rangle, |01\rangle, |10\rangle, |11\rangle\}$.

See that what we want to recreate is the performance of V in the total space. And, it will be applied only in the thermal state when the ancilla is not $|0\rangle$, due to the control gate. Here what we see is a modification of $\mathbb{1} \otimes V$ in which the upper left block has been replaced by the 2×2 identity matrix. With this, what we get is precisely that. One way of looking at it is that the basis vectors in the total space that have the ancilla state $|0\rangle$ associated with them are eigenstate of extended V with eigenvalue 1. In a way, we are saying that as long as the ancilla state is zero it does not modify the state and when it is one it will act on the thermal state.

Continuing, we can evolve the quantum state as in the circuit by applying

$$\begin{aligned} V(\rho_0 \otimes \rho^{eq})V^\dagger &= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & u_{00} & u_{01} \\ 0 & 0 & u_{10} & u_{11} \end{pmatrix} \begin{pmatrix} \frac{p_0}{2} & 0 & \frac{p_0}{2} & 0 \\ 0 & \frac{p_1}{2} & 0 & \frac{p_1}{2} \\ \frac{p_0}{2} & 0 & \frac{p_0}{2} & 0 \\ 0 & \frac{p_1}{2} & 0 & \frac{p_1}{2} \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & u_{00}^* & u_{10}^* \\ 0 & 0 & u_{01}^* & u_{11}^* \end{pmatrix} \\ &= \begin{pmatrix} \frac{p_0}{2} & 0 & \frac{p_0 u_{00}^*}{2} & \frac{p_0 u_{10}^*}{2} \\ 0 & \frac{p_1}{2} & \frac{p_1 u_{01}^*}{2} & \frac{p_1 u_{11}^*}{2} \\ \frac{p_0 u_{00}}{2} & \frac{p_1 u_{01}}{2} & \frac{1}{2}p_0 u_{00} u_{00}^* + \frac{1}{2}p_1 u_{01} u_{01}^* & \frac{1}{2}p_0 u_{00} u_{10}^* + \frac{1}{2}p_1 u_{01} u_{11}^* \\ \frac{p_0 u_{10}}{2} & \frac{p_1 u_{11}}{2} & \frac{1}{2}p_0 u_{00}^* u_{10} + \frac{1}{2}p_1 u_{01}^* u_{11} & \frac{1}{2}p_0 u_{10} u_{10}^* + \frac{1}{2}p_1 u_{11} u_{11}^* \end{pmatrix}. \end{aligned} \tag{4.17}$$

Finally, by measuring the mean values of the Pauli $X \otimes \mathbb{1}$ and $Y \otimes \mathbb{1}$ matrices as the trace of the state evolved times these matrices

$$\begin{aligned} \langle X \rangle = \mathrm{Tr}\left\{V(\rho_0 \otimes \rho^{eq})V^\dagger X \otimes \mathbb{1}\right\} &= \mathrm{Tr}\left\{V(\rho_0 \otimes \rho^{eq})V^\dagger \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}\right\} \\ &= \frac{1}{2}\left(p_0 u_{00} + p_1 u_{11} + p_0 u_{00}^* + p_0 u_{11}^*\right), \\ \langle Y \rangle = \mathrm{Tr}\left\{V(\rho_0 \otimes \rho^{eq})V^\dagger Y \otimes \mathbb{1}\right\} &= \mathrm{Tr}\left\{V(\rho_0 \otimes \rho^{eq})V^\dagger \begin{pmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -i \\ i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{pmatrix}\right\} \\ &= -\frac{1}{2}i\left(p_0 u_{00} + p_1 u_{11} - p_0 u_{00}^* - p_1 u_{11}^*\right). \end{aligned} \tag{4.18}$$

What we obtain is precisely the real and imaginary part of $p_0 u_{00} + p_1 u_{11}$, so that by composing them in the following way $\widetilde{C}_f(u) = \langle X \rangle + i\langle Y \rangle$ we will obtain what we wanted to demonstrate.

The main idea here is that if we have $\mathrm{Tr}\{V\rho\}$ it is possible to access that numerical value through a circuit like the one in figure 4.2 where the mean values of $\langle X\rangle$ and $\langle Y\rangle$ represent the real and imaginary parts respectively.

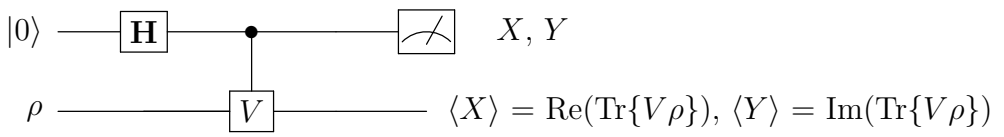


Figure 4.2: Schematic circuit to represent the fundamental idea to enable an experimental proof of the fluctuation theorem. And that is that we can access the quantity $\mathrm{Tr}\{V\rho\}$ by measuring the mean values of the observables X and Y. Since it was shown that: $\langle X\rangle = \mathrm{Re}(\mathrm{Tr}\{V\rho\})$, $\langle Y\rangle = \mathrm{Im}(\mathrm{Tr}\{V\rho\}$.

For our particular case $V = (\mathbb{1}\otimes U^\dagger)(\mathbb{1}\otimes e^{iuG_\tau})'(\mathbb{1}\otimes U)(\mathbb{1}\otimes e^{-iuH_0})'$ where the apostrophe indicates that it is a modification of that tensor product, this is to note that it is a gate control and therefore depends on the state of the ancilla. The driving, on the other hand, is expressed as a product with identity, as it has no control gate associated with it. And calculating the mean value of any of the matrices gives that, i.e for X Pauli matrix $\mathrm{Tr}\left\{V\rho V^\dagger(X\otimes\mathbb{1})\right\} = \mathrm{Tr}\{(\mathbb{1}\otimes U^\dagger)(\mathbb{1}\otimes e^{iuG_\tau})'(\mathbb{1}\otimes U)(\mathbb{1}\otimes e^{-iuH_0})'\rho(\mathbb{1}\otimes e^{iu^*H_0})'(\mathbb{1}\otimes U^\dagger)(\mathbb{1}\otimes e^{-iu^*G_\tau})'(\mathbb{1}\otimes U)(X\otimes\mathbb{1})\}$. Applying the cyclic propertie for the trace: $\mathrm{Tr}\{(\mathbb{1}\otimes e^{iuG_\tau})'(\mathbb{1}\otimes U)(\mathbb{1}\otimes e^{-iuH_0})'\rho(\mathbb{1}\otimes e^{iu^*H_0})'(\mathbb{1}\otimes U^\dagger)(\mathbb{1}\otimes e^{-iu^*G_\tau})'(\mathbb{1}\otimes U)(X\otimes\mathbb{1})(\mathbb{1}\otimes U^\dagger)\}$. If we operate the last three terms: $\mathrm{Tr}\{(\mathbb{1}\otimes e^{iuG_\tau})'(\mathbb{1}\otimes U)(\mathbb{1}\otimes e^{-iuH_0})'\rho(\mathbb{1}\otimes e^{iu^*H_0})'(\mathbb{1}\otimes U^\dagger)(\mathbb{1}\otimes e^{-iu^*G_\tau})'\underbrace{(\mathbb{1}X\mathbb{1}\otimes U\mathbb{1}U^\dagger)}_{X\otimes\mathbb{1}}\}$. As we can see, rotation due to one driving has no effect on the mean values. This is why the unitary rotation associated with $U^\dagger$ is not included in the circuit of figure 4.1.

However, in order to prepare the circuit, it must be t aken into account that quantum computers can only prepare pure states. Therefore, it is interesting to express the characteristic function as follows

$$\widetilde{C}_f(u) = \sum_{k=0}^{1} p_k \mathrm{Tr}\{U^\dagger e^{iuG_\tau} U e^{-iuH_0}|k\rangle\langle k|\}. \tag{4.19}$$

Where the state has been considered to be diagonal in the computational basis $\{|0\rangle, |1\rangle\}$ and then the p_k would be the populations of the state. Thus an interesting way to simulate the thermal state would be to run two circuits each with one ancilla and the corresponding states $|0\rangle$ and $|1\rangle$. Then the average values of X and Y would be calculated, and finally the factors p_k would be taken into account.

For the backward characteristic function, the procedure is quite similar except that it has to be taken into account that transformations like e^{-iuH_0} and e^{iuG_τ} are not unitary. So to work with them it is convenient to first make a decomposition with a Pauli String.

The key idea of this is to be able to put any matrix A belonging to the vector space of matrices of order 2×2 of complex coefficients, $\mathcal{M}_{2\times 2}(\mathbb{C})$, as a linear combination of Pauli matrices: $A = \sum_{k=0}^{3} = \alpha_k\sigma_k$. Where the coefficients α_k can be calculated very easily just by taking the trace times one Pauli matrix

$$\begin{aligned}\mathrm{Tr}\left\{A\sigma_1\right\} &= \mathrm{Tr}\left\{\alpha_0\sigma_0\sigma_1 + \alpha_1\sigma_1\sigma_1 + \alpha_2\sigma_2\sigma_1 + \alpha_3\sigma_3\sigma_1\right\} \\ &= \alpha_1 \mathrm{Tr}\left\{\mathbb{1}\right\} + \sum_{j=1}^{3} \cancelto{0}{\mathrm{Tr}\{e_j\sigma_j\}} = 2\alpha_1.\end{aligned} \tag{4.20}$$

Thus the coefficient α_j takes the form $\alpha_j = 1/2\mathrm{Tr}\{A\sigma_j\}$. Where the relationship $\sigma_i\sigma_j = i\epsilon_{ijk}\sigma_k$ and $\mathrm{Tr}\{\sigma_k\} = 0$ has been taken into account. Then, using this feature we can write the backward characteristic function as follows

$$\widetilde{C}_b(-u + i\beta) = \sum_{k,l} = \alpha_k^{(0)}\alpha_l^{(\tau)}F_{kl}. \tag{4.21}$$

Writing the rotations as, $e^{\beta H_0} = \sum_{k=0}^{3}\alpha_k^{(0)}\sigma_k$ and $e^{\beta G_\tau} = \sum_{l=0}^{3}\alpha_l^{(\tau)}\sigma_l$, where the coefficients $\alpha_k^{(0)}$ and $\alpha_l^{(\tau)}$ take the following form $\alpha_k^{(0)} = \mathrm{Tr}\{e^{-\beta H_0}\sigma_k\}$, $\alpha_l^{(\tau)} = \mathrm{Tr}\{e^{\beta G_\tau}\sigma_l\}$. And F_{kl} would be

$$F_{k\ell} \equiv \mathrm{tr}\left\{U\sigma_k e^{-iuH_0}U^\dagger\sigma_\ell e^{iuG_\tau}\tilde{\rho}_\tau\right\}. \tag{4.22}$$

So having access to the coefficients $\alpha's$ classically the coefficients F_{kl} could be calculated with the following quantum circuit (see figure 4.3). Therefore be able to calculate the backward characteristic function by composing them as in equation 4.21.

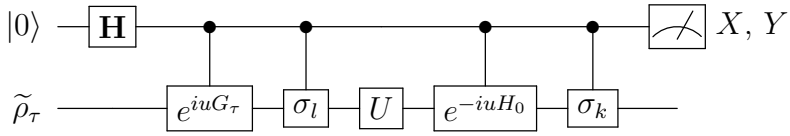


Figure 4.3: Quantum circuit for calculating the coefficients F_{kl} in the backward characteristic function. Where we can see that all the unitary rotations acting on $\widetilde{\rho}_\tau$ are applied except the one associated with the hermitic conjugate of the time evolution operator for the same reasons as for the other circuit.

With all these ideas the authors of [2] were able to compute the symmetry relation above, see equation 4.13. Where for a given initial Hamiltonian and driving the relation became

$$R_{true} = \frac{\widetilde{C}_f(1)}{\widetilde{C}_b(-1 + 0.5i)} = 0.433167. \tag{4.23}$$

Quantum circuits such as those in figures 4.1 and 4.3 were developed to compute the characteristic functions. Each was run about 20000 times to obtain a value for R_{true}. This process was performed N times and the average was taken as a good estimator. Thus it was seen that, as the number of repetitions increased, the relative error decreased. It became 0.12 % with $N = 100$. This is low enough to consider that the fluctuation theorem of the OTM scheme could be proved.

Hence the power of the characteristic functions and how they allowed us to access an experimental proof of the fluctuation theorem under the OTM scheme is evident. The key

was to realize that the rotations present in the expression 4.12 could be carried out on a quantum computer by performing these same operations on qubits.

Conclusion

In conclusion, the probabilistic interpretation of the work has been evident throughout the project. Thanks to this, Jarzynsky's equality has been presented and the importance of having a series of equalities for work-related quantities in non-equilibrium processes has been analyzed. We have come to the conclusion that where elementary thermodynamics only yields inequalities for non-equilibrium processes, this probabilistic interpretation yields equalities independent of the type of process, i.e. non-quasi-static.

In addition to this, the concepts of the work distribution function and characteristic function have been presented under the two most common work measurement schemes in quantum mechanics, the two-time measurement scheme (TTM) and the one-time measurement scheme (OTM). Including a demonstration of Jarzynsky's equality for the case of a quantum system of unitary dynamics under the TTM scheme. And, from this equality, it has been possible to generalize the second law of thermodynamics for fluctuating systems, where what we obtain is the same relation but for the mean values. This does not prevent local violations of the second principle from occurring. These violations have been seen in the magnetic resonance experiment (N independent spins subject to a uniform magnetic field and a time-dependent perturbation perpendicular to it) which occurred when the perturbation caused transitions from the anti-aligned to the aligned spin state to the magnetic field. It has been shown in figures 3.3 how the probability of these decreases with the number of constituents, which explains why we do not perceive them on the macroscopic scale.

In relation to the OTM scheme, we have shown that it is indeed a non-destructive TTM scheme, due to the fact that in the second measure, the coherences are maintained. Also from this, we have been able to derive a modified Jarzynsky equality in which the informational cost of the measure is accounted for and we have obtained a second law for the mean value of work in non-equilibrium processes which has a much better lower bound than in TTM scheme since it includes the measurement as a thermodynamic process. This is reflected in the appearance of an extra term in the equality that has to do with how different the state evolved by the protocol is from the thermal state it would tend to be if we let the system relax.

On the other hand, we have explained the connection between characteristic functions and the possibility of obtaining an experimental proof of the fluctuation theorem on a quantum computer. It has been explained how the rotations acting on the thermal states in the expression of the characteristic function can be operations realizable by a quantum computer where the quantum circuits for them have been given. And, therefore, obtain the character-

istic function from measuring the Pauli matrices X and Y in the evolved state qubit ancilla and target state.

Finally, this work has been an introduction to non-equilibrium thermodynamics, which is an area where much remains to be explored. We have limited ourselves to closed quantum systems, which, although feasible in many scenarios, the reality is that many resources are currently being invested in the study of open systems. We also had a brief encounter with how quantum technologies can serve as experimental tests of certain theories. We worked a little on how quantum algorithms work.

Bibliography

[1] Wellington L Ribeiro, Gabriel T Landi, and Fernando L Semião. Quantum thermodynamics and work fluctuations with applications to magnetic resonance. *American Journal of Physics*, 84(12):948–957, 2016.

[2] Kenji Maeda, Tharon Holdsworth, Sebastian Deffner, and Akira Sone. Detailed fluctuation theorem from the one-time measurement scheme. *Physical Review A*, 108(5), November 2023.

[3] Sebastian Deffner, Juan Pablo Paz, and Wojciech H. Zurek. Quantum work and the thermodynamic cost of quantum measurements. *Physical Review E*, 94(1), July 2016.

[4] Werner Lauterborn. Acoustic chaos. In Robert A. Meyers, editor, *Encyclopedia of Physical Science and Technology (Third Edition)*, pages 117–127. Academic Press, New York, third edition edition, 2003.

[5] Daniel Alonso Ramírez and Antonia Ruiz García. Lecture notes in statistical mechanics, November 2019.

[6] K. W. Plumb, Hitesh J. Changlani, A. Scheie, Shu Zhang, J. W. Krizan, J. A. Rodriguez-Rivera, Yiming Qiu, B. Winn, R. J. Cava, and C. L. Broholm. Continuum of quantum fluctuations in a three-dimensional s = 1 heisenberg magnet. *Nature physics*, 15(1):54–59, 2019.

[7] C. Jarzynski. Nonequilibrium equality for free energy differences. *Phys. Rev. Lett.*, 78:2690–2693, Apr 1997.

[8] C. Jarzynski. Equilibrium free-energy differences from nonequilibrium measurements: A master-equation approach. *Phys. Rev. E*, 56:5018–5035, Nov 1997.

[9] Gavin E Crooks. Nonequilibrium measurements of free energy differences for microscopically reversible markovian systems. *Journal of Statistical Physics*, 90:1481–1487, 1998.

[10] Gavin E Crooks. Path-ensemble averages in systems driven far from equilibrium. *Physical review E*, 61(3):2361, 2000.

[11] Michele Campisi, Peter Hänggi, and Peter Talkner. Colloquium: Quantum fluctuation relations: Foundations and applications. *Reviews of Modern Physics*, 83(3):771, 2011.

[12] Carlos Alexandre Brasil and Leonardo Andreta de Castro. Understanding the pointer states. *European Journal of Physics*, 36(6):065024, September 2015.

Appendix A

Unitary operators lead to entropy constant

In this appendix it will be shown that unitary operators keep the entropy constant and are therefore the basis for describing non-dissipative systems.

Proof. Let a quantum state be defined from its density matrix $\rho(t)$ at time t. Let us take as a reference the Von Neumann entropy at $t = 0$:

$$S(0) = -\mathrm{Tr}\{\rho(0) ln \rho(0)\}. \tag{A.1}$$

At time t, taking into account the evolution of the density operator $\rho(t) = U(t)\rho(0)U^\dagger(t)$. We will obtain:

$$S(t) = -\mathrm{Tr}\{\rho(t) ln \rho(t)\} = -\mathrm{Tr}\{U(t)\rho(0)U^\dagger(t) ln(U(t)\rho(0)U^\dagger(t))\}. \tag{A.2}$$

Doing a Tylor series expansion:

$$f(U(t)\rho(0)U^\dagger(t)) = f_0 + f_1\, U(t)\rho(0)U^\dagger(t) + f_2\, U(t)\rho(0)\underbrace{U^\dagger(t)\cdot U(t)}_{1}\rho(0)U^\dagger(t) + ... \tag{A.3}$$

$$f(U(t)\rho(0)U^\dagger(t)) = f_0 + f_1\, U(t)\rho(0)U^\dagger(t) + f_2\, U(t)\rho(0)\cdot\rho(0)U^\dagger(t) + ... = U(t) f(\rho(0))U^\dagger(t). \tag{A.4}$$

Inserting the result of equation A.4 in equation A.1 with $f(\rho(0)) = ln(\rho(0))$:

$$S(t) = -\mathrm{Tr}\{U(t)\rho(0)\underbrace{U^\dagger(t)U(t)}_{1} ln(\rho(0))U^\dagger(t)\}. \tag{A.5}$$

Finally, using the cyclic trace property, $\mathrm{Tr}\{\mathbf{ABC}\} = \mathrm{Tr}\{\mathbf{BCA}\} = \mathrm{Tr}\{\mathbf{CAB}\}$, Finally:

$$S(t) = -\mathrm{Tr}\{U(t)\rho(0)ln(\rho(0))U^\dagger(t)\} = -\mathrm{Tr}\{\rho(0)ln(\rho(0))\underbrace{U^\dagger(t)U(t)}_{1}\} = -\mathrm{Tr}\{\rho(0)ln\rho(0)\} = S(0). \tag{A.6}$$

So it is shown that the unitary operators do not modify the entropy. □

Appendix B

Average value of Work

In this appendix it will be shown that the mean value of the work in the particular protocol of chapter 2 is the difference of the mean values of the energy at the beginning and at the end of the protocol.

Proof. Consider the expression obtained in chapter 2 for the characteristic function (see equation 2.8):

$$G(r) = \langle e^{irW} \rangle = \mathrm{Tr}\{U^\dagger(\tau) e^{irH_f} U(\tau) e^{-irH_i} \rho_{th}\}. \tag{B.1}$$

Doing a Maclaurin expansion in the variable r of the operators e^{irH_f} and e^{irH_i}:

$$G(r) = \mathrm{Tr}\{U^\dagger(\tau)[1 + irH_f + \mathcal{O}\left(r^2\right)]U(\tau)[1 - irH_i + \mathcal{O}\left(r^2\right)]\rho_{th}\}. \tag{B.2}$$

Comparing with the expansion in equation B.1 at left side of the second equality:

$$\begin{aligned} G(r) = \langle e^{irW} \rangle &= 1 + ir\langle W \rangle + \mathcal{O}(r^2) \\ &= \mathrm{Tr}\{\underbrace{U^\dagger U}_{\mathbb{1}} \rho_{th} - ir \underbrace{U^\dagger U}_{\mathbb{1}} H_i \rho_{tau} + irU^\dagger H_\tau U \rho_{th} + \mathcal{O}\left(r^2\right)\}. \end{aligned} \tag{B.3}$$

Remaining only to first order in r. We obtain:

$$\langle W \rangle = \mathrm{Tr}\left\{U^\dagger H_\tau U \rho_{th}\right\} - \mathrm{Tr}\{H_i \rho_{th}\}. \tag{B.4}$$

Now, applying the following relations:

$$\begin{aligned} &\mathrm{Tr}\left\{U^t H_\tau U \rho_{th}\right\} = \mathrm{Tr}\left\{H_\tau U \rho_{th} U^+\right\} = \mathrm{Tr}\{H_\tau \rho_\tau\} = \langle H_\tau \rangle_\tau \\ &\mathrm{Tr}\{H_i \rho_{th}\} = \langle H_i \rangle_0 . \end{aligned} \tag{B.5}$$

Where in the first equality of the first line the cyclic property of the trace has been used. In the following equality the evolution of the density operator according to *driving* $\rho_{th} = U^\dagger \rho_\tau U$ has been used. And, the expression for the mean value of operators in mixed statistical states:

$$\langle A \rangle_t = \mathrm{Tr}\left\{A\rho\right\}. \tag{B.6}$$

Therefore, we can conclude that:

$$\langle W \rangle = \langle H_\tau \rangle_\tau - \langle H_0 \rangle_0. \tag{B.7}$$

□

Appendix C

Calculation of Γ_k coefficients

Given the expression for the characteristic function of the N-particle system, equation 3.25,

$$\mathcal{G}(r) = (b_0 + b_+ e^{iB_0 r} + b_- e^{-iB_0 r})^N, \tag{C.1}$$

we can use Newton's binomial formula to account for the coefficients Γ_k. That is, we will use $(a+b)^N = \sum_{k=0}^{N} \binom{N}{k} a^k b^{N-k}$, as follows:

$$\begin{aligned}(a+b+c)^N = \sum_{k=0}^{N} \binom{N}{k} (a+b)^k c^{N-k} = \sum_{k=0}^{N} c^{N-k} \binom{N}{k} \sum_{l=0}^{k} \binom{k}{l} a^l b^{k-l} = \\ = \sum_{k=0}^{N} \sum_{l=a}^{k} \binom{N}{k} \binom{k}{l} c^{N-k} b^{k-l} a^l.\end{aligned} \tag{C.2}$$

For our particular case in equation C.1, $a = b_0, b = b_+ e^{irB_0}$ and $b_- e^{-irB_0}$, thus, the expression C.2 would be:

$$\begin{aligned}\mathcal{G}(r) = \sum_{k=0}^{N} \sum_{l=0}^{k} \binom{N}{k} \binom{k}{l} b_-^{N-k} b_+^{k-l} b_0^l \underbrace{e^{-i(N-k)B_0 r} e^{i(k-l)B_0 r}}_{e^{i(N-k-k+l)B_0 r} = e^{-i(N+l-2k)B_0 r}} = \\ \sum_{k=0}^{N} \sum_{l=0}^{k} \binom{N}{k} \binom{k}{l} b_-^{N-k} b_+^{k-l} b_0^l \, e^{-i(N+l-2k)B_0 r}.\end{aligned} \tag{C.3}$$

So once we do the inverse Fourier transform, we arrive at a very simple expression for the probability distribution of the work:

$$
\begin{aligned}
P(\mathcal{W}) &= \frac{1}{2\pi}\int_{-\infty}^{\infty} dr \mathcal{G}(r) e^{-i\mathcal{W}r} = \\
&= \sum_{k=0}^{N}\sum_{l=0}^{k} \binom{N}{k}\binom{k}{l} b_{-}^{N-k} b_{+}^{k-l} b_{0}^{l} \underbrace{\left(\frac{1}{2\pi}\right)\int_{-\infty}^{\infty} dr e^{-i(\mathcal{W}+(N+l-2k)B_0 r)r}}_{\delta(\mathcal{W}+(N+l-2k)B_0 r)} \qquad \text{(C.4)} \\
&= \sum_{k=0}^{N}\sum_{l=0}^{k} \binom{N}{k}\binom{k}{l} b_{-}^{N-k} b_{+}^{k-l} b_{0}^{l}\, \delta(\mathcal{W}+(N+l-2k)B_0 r).
\end{aligned}
$$

Where to obtain the coefficients in k we would have to change the double summation of k and l to a single sum in a new variable k which will have the values $N+l-2k$ and will go from N to $-N$. However for our purposes this expression is more than valid to obtain the results of the figures 3.3.

Appendix D

Derivation of $\tilde{H}$ for one spin problem

In this appendix we will show that under the interaction picture the interaction Hamiltonian corresponding to the Schrödinger Hamiltonian of equation 3.4, that is,

$$H(t) = -\frac{B_0}{2}\sigma_z - \frac{B_1}{2}(\sigma_x \sin\omega t + \sigma_y \cos\omega t). \tag{D.1}$$

It is:

$$\tilde{H} = -\frac{(B_0 - \omega)}{2}\sigma_z - \frac{B_1}{2}\sigma_y. \tag{D.2}$$

To demonstrate this we will follow from the evolution equation of the time evolution operator, which is written as, $i\partial_t U(t) = H(t)U(t)$. Then, using the relation $U = e^{iwt\sigma_z/2}\tilde{U}$, in the evolution equation above:

$$i\partial_t U(t) = i\left[i\frac{\omega\sigma_z}{2}e^{i\frac{\omega t\sigma_z}{2}}\tilde{U}(t) + e^{\frac{i\omega t\sigma_z}{2}} + \tilde{U}(t)\right] = H(t)\,e^{i\frac{\omega toz}{2}}\tilde{U}. \tag{D.3}$$

Now let us separate on the left and on the right the parts that depend on the partial of $\tilde{U}$ and in which a appears only multiplying on the right. This is to put it in the form of the evolution equation in the Schrödinger picture:

$$i\partial_t\tilde{U}(t) = \left[e^{-i\omega t\sigma_z/2}H(t)\,e^{i\omega t\sigma_z/2} + \frac{\omega}{2}\sigma_z\right]\tilde{U}(t). \tag{D.4}$$

It follows that $\tilde{U} = e^{-i\omega t\sigma_z/2}H(t)\,e^{i\omega t\sigma_z/2} + \frac{\omega}{2}\sigma_z$. Let us then develop this expression to find a simpler form that will eliminate the time evolution completely, we will call $\alpha = \omega t\sigma_z/2$. Therefore:

$$\begin{aligned}\tilde{H} = e^{-i\alpha\sigma_z}H(t)e^{i\alpha\sigma_z} + \frac{\omega}{2}\sigma_z = \\ &= e^{-i\alpha\sigma_z}\left[-\frac{B_0}{2}\sigma_z - \frac{B_1}{2}(\sigma_x S + \sigma_y C)\right]e^{i\alpha\sigma_z} + \frac{\omega}{2}\sigma_z \\ &= -\frac{B_0}{2}\sigma_z - e^{-i\alpha\sigma_z}\frac{B_1}{2}(\sigma_x S + \sigma_y C)e^{i\alpha\sigma_z} + \frac{\omega}{2}\sigma_z.\end{aligned} \tag{D.5}$$

Where C and S represent the $\cos\omega t$ and $\sin\omega t$ respectively. At this point we need to see how it acts $e^{i\alpha\sigma_z}$ on σ_x and σ_y. So, we will start by using the useful relationship from chapter 3, the equation 3.9. So, we can put $e^{-i\alpha\sigma_z} = \mathbb{1}\cos\alpha - i\sigma_z\sin\alpha$. Continuing:

$$e^{-i\alpha\sigma_z}\frac{B_1}{2}(\sigma_x S + \sigma_y C)e^{i\alpha\sigma_z} = (\mathbb{1}\cos\alpha - i\sigma_z\sin\alpha)\begin{Bmatrix}\sigma_x\\ \sigma_y\end{Bmatrix}(\mathbb{1}\cos\alpha + i\sigma_z\sin\alpha)\,. \tag{D.6}$$

Therefore, by distributing and pooling the terms that remain with σ_x and σ_y:

$$\begin{aligned}\sigma_x: &\quad \sigma_x\cos^2\alpha + i\cos\alpha\sin\alpha\sigma_x\sigma_z - i\sin\alpha\cos\alpha\sigma_z\sigma_x + \sin^2\alpha\sigma_z\sigma_x\sigma_z\\ \sigma_y: &\quad \sigma_y\cos^2 x + i\cos\alpha\sin\alpha\sigma_y\sigma_z - i\sin\alpha\cos\alpha\sigma_z\sigma_y + \sin^2\alpha\sigma_z\sigma_y\sigma_z.\end{aligned} \tag{D.7}$$

So taking into account the cyclic relationships for Pauli matrices $\sigma_i\sigma_j = i\varepsilon_{ijk}\sigma_k$, we can put the above expression as:

$$\begin{aligned}\sigma_x: &\quad \sigma_x\cos^2\alpha + i\cos\alpha\sin\alpha(-i\sigma_y) - i\sin\alpha\cos\alpha(\sigma_y) + \sin^2\alpha\sigma_x\\ \sigma_y: &\quad \sigma_y\cos^2 x - i\cos\alpha\sin\alpha\sigma_x - i\sin\alpha\cos\alpha(-i\sigma_x) - \sin^2\alpha\sigma_y.\end{aligned} \tag{D.8}$$

Now let's do the reverse and call C and S to $\cos\alpha$ and $\sin\alpha$. Going back to the equation D.6 and substituting:

$$\begin{aligned}\tilde{H} &= -\frac{(B_0 - W)}{2}\sigma_z - \frac{B_1}{2}\sin\omega t(\sigma_x C^2 + CS\sigma_y + SC\sigma_y - S^2\sigma_x)\\ &\qquad - \frac{B1}{2}\cos\omega t\left(\sigma_y C^2 - CS\sigma_x - SC\sigma_x - S^2\sigma_y\right).\\ &= \frac{(B_0 - W)}{2}\sigma_z\\ &- \frac{B_1}{2}\sin\omega t[\sigma_x\underbrace{(C(\omega t/2)^2 - S(\omega t/2)^2)}_{C^2(\omega t/2)} + \underbrace{2C(\omega t/2)S(\omega t/2)}_{S(\omega t/2)}\sigma_y]\\ &- \frac{B_1}{2}\cos\omega t[\sigma_y\underbrace{(C(\omega t/2)^2 - S(\omega t/2)^2)}_{C^2(\omega t/2)} - \underbrace{2C(\omega t/2)S(\omega t/2)}_{S(\omega t/2)}\sigma_x]\\ &= \frac{-(B_0 - W)}{2} - \frac{B_1}{2}S\left(\sigma_x C + \sigma_y S\right) - \frac{B_1}{2}C\left(\sigma_y C - \sigma_x S\right)\\ &= -\frac{B_0 - \omega}{2}\sigma_z - \frac{B_1}{2}\left[\cancel{\sigma_x SC} + S^2\sigma_y + \sigma_y C^2 - \cancel{CS\sigma_x}\right]\\ &= -\frac{B_0 - \omega}{2} - \frac{B_1}{2}\sigma_y.\end{aligned}$$

We finally arrived at a time-independent expression, which is what was intended.