

Universidad de La Laguna

TRABAJO DE FIN DE GRADO

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**INTRODUCTION OF WORK IN QUANTUM
MECHANICS**

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1 Motivation

The main motivation for this project was to understand classical work within the framework of quantum mechanics. We seek to understand what it means work in a quantum system and how to compute it. To achieve this, it is necessary to grasp the definition of work in thermodynamics and tailor it to the particular quantum system at hand. Once the definition of work in a quantum system has been established, the next goal is to determine the possible values of work for a given Hamiltonian, as well as the average work. This is done through a two-point measurement protocol [11] that includes initial and final energy measurements. Finally, the project aims to study the probability distribution and related statistical variables and to explore the implications of increasing the number of particles in the system. Understanding the nature of work in quantum systems and the influence of different numbers of particles is important for various applications in quantum technology and to advance our knowledge of basic physical processes.

2 Chapter 1: Introduction

Abstract

Comenzaremos haciendo una introducción histórica de la termodinámica, la mecánica cuántica y la mecánica estadística; todo ello para poder apreciar posteriormente su relación entre sí y con los sistemas cuánticos que vamos a tratar. Posteriormente introduciremos el sistema cuántico a tratar para hacer primero, una diferenciación entre las variables de interés (trabajo y calor) y su forma en este sistema; y segundo, tratar dos ejemplos para ver el comportamiento de estas variables, a priori, termodinámicas en dichos sistemas cuánticos. Para esto último nos serviremos principalmente de cálculo matricial básico y de métodos numéricos para resolver sistemas de ecuaciones diferenciales, apoyándonos en las figuras mostradas para sacar algunas conclusiones.

Algunas expresiones que se derivan en este apartado serán usadas en siguientes secciones con tal de facilitar el desarrollo matemático.

2.1 Historical introduction

The fields of thermodynamics, statistical mechanics, and quantum mechanics are fundamental branches of physics that have revolutionized our understanding of the natural world. Each of these fields of study has its history of development, but they are deeply interconnected, with the concepts and principles of one influencing and enriching the others. In this introduction, we will explore the historical context of thermodynamics, statistical mechanics, and quantum mechanics, as well as their relationships and applications in the field of quantum systems.

- Thermodynamics:** [1] The study of thermodynamics began in the 19th century when scientists investigated the behavior of heat and energy. The Industrial Revolution sparked the need for efficient engines, leading to the development of the First and Second Laws of thermodynamics. In the mid-19th century, Rudolf Clausius and Lord Kelvin, among others, formulated these laws, which laid the foundation for the principles governing energy conversion and heat transfer in macroscopic systems. It was also at this time that Carnot introduced us to the first modern definition of work: a weight lifted by a height. Thermodynamics has become essential for many different practical applications, including steam engines, refrigeration, and power generation.

First Law of Thermodynamics:[2] *In an isolated adiabatic system that evolves from an initial state A to another final state B , the work done does not depend on the type of work or the process followed.*

$$\Delta U = Q - W \quad (1)$$

Where U is the internal energy of the (isolated) system, Q is the amount of heat supplied to the system and W is the work done by the system.

- Quantum mechanics:** [3] The advent of quantum mechanics in the early 20th century revolutionized physics. Scientists such as Max Planck, Albert Einstein, Niels Bohr, Erwin Schrödinger and Werner Heisenberg have made pioneering contributions in this field like Schrödinger equation or Heisenberg uncertainty principle. Quantum mechanics introduces the idea that particles exhibit wave-particle duality and that their properties are described by wave functions. These wave functions challenged classical notions of determinism and fundamentally changed our understanding of matter and energy at the microscopic level.

Schrödinger equation:[4] *The Schrödinger equation gives the quantized energies of the system and gives the form of the wave function so that other properties can be calculated.*

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = H(t) |\psi(t)\rangle \quad (2)$$

Where i is the imaginary unit, \hbar is the reduced Planck constant, ψ is the wave function of the quantum system, and H is the Hamiltonian differential operator.

- Statistical mechanics:** [5] While thermodynamics provides a macroscopic understanding of energy, statistical mechanics emerged in the late 19th century to explain the microscopic origin of macroscopic properties. Scottish physicist James Clerk Maxwell and the Austrian physicist Ludwig Boltzmann played important roles in the development of statistical mechanics. Boltzmann's statistical interpretation of entropy linked the concepts of probability

and thermodynamics, allowing for a deeper understanding of the behavior of large particle systems. Statistical mechanics is the bridge between the microscopic world of individual particles and the macroscopic world described by thermodynamics.

The connection between thermodynamics, statistical mechanics, and quantum mechanics became apparent as physicists explored the behavior of quantum systems. Quantum statistical mechanics [6] was developed to describe the statistical behavior of particles according to quantum principles. This framework provides an overview of phenomena governed by the Bose-Einstein and Fermi-Dirac statistics, which characterize the behavior of particles with integer (bosons) and half-integer spins (fermions), respectively. Furthermore, the principles of thermodynamics, such as the conservation of energy and entropy, find new manifestations in the quantum field. Quantum thermodynamics is an emerging field that studies the exchange of energy and heat in quantum systems, in which quantum fluctuations and coherence play an important role. The application of these concepts is crucial in various fields, including quantum computing, quantum information theory, and quantum optics. Understanding and manipulating quantum systems requires a deep understanding of the statistical behavior and the quantum nature of the particles involved.

In sum, the historical development of thermodynamics, statistical mechanics, and quantum mechanics has dramatically shaped our understanding of the physical world. The interactions between these fields have allowed us to explore the behavior of quantum systems, opening new frontiers in technology, computing, and fundamental physics. Ongoing research in these areas continues to advance our knowledge and pave the way for future advances in quantum science and technology. In this final degree project, we are precisely going to treat thermodynamic variables in isolated quantum systems. We will give special emphasis to the study of work and its properties in these systems.

2.2 Quantum Work driven in a isolated system

[7] We have a quantum system in interaction with a thermal bath, in this way the Hamiltonian will be the sum of both plus the interaction potential between them, all of them will depend on time:

$$H(t) = H_S(t) + H_B(t) + V_{SB}(t) \quad (3)$$

The quantum average will be the trace of the Hamiltonian and the density matrix, in such a way that deriving:

$$\begin{aligned} \langle H(t) \rangle &= \text{Tr}(\rho(t)H(t)) \implies \\ \frac{d\langle H(t) \rangle}{dt} &= \text{Tr}(\dot{\rho}(t)H(t)) + \text{Tr}(\rho(t)\dot{H}(t)) \end{aligned}$$

We could associate this with the 1st Law of Thermodynamics 1, but it would be necessary to identify which sum corresponds to work and which to other form of energy. To do this, we assume an isolated system, that is, there is no heat loss or gain. This Hamiltonian will have the form: $H_S(t) = f(t)\sigma_z$. In an example later we will shape the function and apply some initial conditions to better visualize each term.

On the other hand, it is known that the temporal evolution of the density of states is given by the Liouville-von Neumann equation [8]:

$$i\hbar \frac{\partial \rho}{\partial t} = [H, \rho] \quad (4)$$

Whereas $\rho \rightarrow \{\rho_{11}, \rho_{12}, \rho_{21}, \rho_{22}\}$ we will have 4 differential equations, two of them for the populatios and two are coherences.

With this equation we can analyze the traces obtained before and see what happens for the isolated case, the first addend:

$$\begin{aligned} \text{Tr}(\dot{\rho}(t)H_S) &= \text{Tr}\left(\frac{[H_S, \rho]}{i\hbar} H_S\right) = \frac{1}{i\hbar} \text{Tr}((H_S\rho - \rho H_S)H_S - H_S(H_S\rho - \rho H_S)) = \\ &= \frac{1}{i\hbar} \text{Tr}(\cancel{H_S\rho H_S} - \rho H_S^2 - H_S^2\rho - \cancel{H_S\rho H_S}) = \frac{1}{i\hbar} \text{Tr}(\rho \cancel{H_S^2} - \rho \cancel{H_S^2} - \cancel{H_S^2\rho} + \cancel{H_S^2\rho}) = 0 \end{aligned} \quad (5)$$

And the second addend:

$$\text{Tr}(\rho(t)\dot{H}_S) = \text{Tr}(\rho(t)\dot{f}(t)\sigma_z) = \dot{f}(t)\text{Tr}(\rho(t)\sigma_z) \quad (6)$$

Therefore, the first addend, being null, knowing that we are in the specific case of an isolated system, corresponds to heat, and the second, assuming all the energy of the system, corresponds to work.

Now, we are going to analyze two examples to show the procedure to follow to obtain the thermodynamic variables of the quantum system.

• **Example 1:**

Suppose that our time-dependent function is $f(t) = \sin(\omega t)$ and that the initial condition of the system is: $|\psi\rangle\langle\psi| = \left(\frac{|1\rangle - |2\rangle}{\sqrt{2}}\right) \left(\frac{\langle 1| - \langle 2|}{\sqrt{2}}\right)$.

In that case, the initial density matrix will be:

$$\rho(0) = \frac{1}{2} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \quad (7)$$

Now, using 4 and operating conveniently we arrive at:

$$i\hbar \frac{\partial \rho}{\partial t} = f(t) \begin{pmatrix} 0 & 2\rho_{12} \\ -2\rho_{21} & 0 \end{pmatrix} = \sin(\omega t) \begin{pmatrix} 0 & 2\rho_{12} \\ -2\rho_{21} & 0 \end{pmatrix} \quad (8)$$

Therefore, the diagonal terms of the density matrix will be constant, while the non-diagonal ones will not. In fact, having the same initial conditions in this case, they will be the same with a change of sign, leaving:

$$\rho_{12}(t) = \rho_{21}(t)^* = \rho_{12}(0) \exp\left(\frac{2}{i\hbar} \int_0^t \sin(\omega s) ds\right) = -\frac{1}{2} \exp\left(-\frac{2}{i\hbar \omega} \cos(\omega t)\right) \quad (9)$$

Now with this, we can calculate all the terms mentioned before, for example:

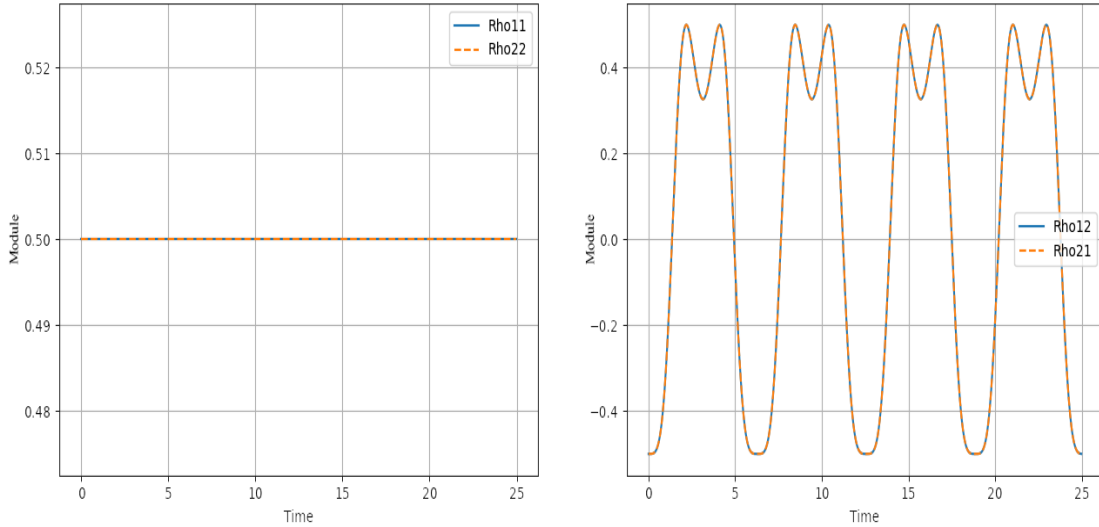
$$\langle H(t) \rangle = \text{Tr}(\rho(t)H(t)) = \sin(\omega t) \text{Tr} \left(\begin{pmatrix} 1/2 & -\rho_{12} \\ \rho_{21} & -1/2 \end{pmatrix} \right) = 0$$

This makes sense since the function is a sine and the initial populations are equal, the average energy will be zero. The terms of heat and work will remain:

$$Q(t) = \text{Tr}(\dot{\rho}(t)H(t)) = \frac{\sin(\omega t)}{i\hbar} \text{Tr} \left(\begin{pmatrix} 0 & 2\rho_{12} \\ 2\rho_{21} & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \right) = 0$$

$$W(t) = \text{Tr}(\rho(t)\dot{H}(t)) = \omega \cos(\omega t) \text{Tr} \left(\begin{pmatrix} 1/2 & -\rho_{12} \\ -\rho_{12} & -1/2 \end{pmatrix} \right) = 0$$

On average they are null, this is because the diagonal terms assume the same weights, and as we saw before, these terms will not evolve over time, obtaining zero work for any time t. That is, the work is zero since the trace of the Hamiltonian is zero at all times t. Now, if we represent by components:



(a) Diagonal components $w = \hbar = 1$. (b) Anti-diagonal components $w = \hbar = 1$.

Figure I: Components of density operator.

It can be observed that the components of the diagonal are constant, as expected, for the antidiagonal they do vary periodically but they are equal. It is notorious that the variation of the energy in time will be equal to the work, which in this case is zero.

• **Example 2:**

Suppose now that the initial condition is the same as in example one but our hamiltonian is $H = \frac{\lambda}{2}\sigma_x + \frac{f(t)}{2}\sigma_z$.

In matrix form we would have the following:

$$H = \frac{1}{2} \begin{pmatrix} \sin(wt) & \lambda \\ \lambda & -\sin(wt) \end{pmatrix} \quad (10)$$

As in the previous example, using 4 and operating the matrices, we obtain:

$$i\hbar \frac{\partial \rho}{\partial t} = \frac{1}{2} \begin{pmatrix} \lambda(\rho_{21} - \rho_{12}) & 2 \sin(wt)\rho_{12} + \lambda(\rho_{22} - \rho_{11}) \\ -2 \sin(wt)\rho_{12} - \lambda(\rho_{22} - \rho_{11}) & -\lambda(\rho_{21} - \rho_{12}) \end{pmatrix} \quad (11)$$

This system is not easy to solve but although we cannot obtain the exact solution, we can approximate it using numerical methods, in this case, the Runge-Kutta of order 4:

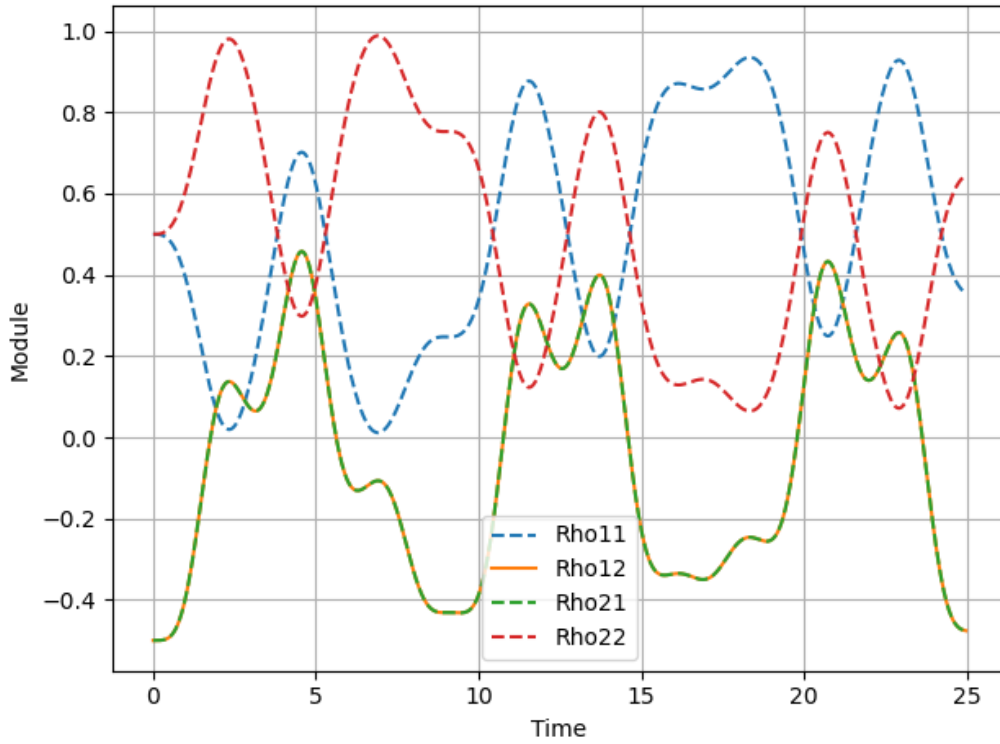


Figure II: Numerical solution of density operator ($\lambda = \hbar = w = 1$).

In the same way as in the previous example, we can calculate the heat and work:

$$Q(t) = \frac{1}{4i\hbar} \text{Tr} \begin{pmatrix} \lambda(\rho_{21} - \rho_{12}) & 2 \sin(wt)\rho_{12} + \lambda(\rho_{22} - \rho_{11}) \\ -2 \sin(wt)\rho_{12} - \lambda(\rho_{22} - \rho_{11}) & -\lambda(\rho_{21} - \rho_{12}) \end{pmatrix}$$

$$\begin{pmatrix} \sin(wt) & \lambda \\ \lambda & -\sin(wt) \end{pmatrix} = 0$$

$$W(t) = \text{Tr} \left(\begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} \begin{pmatrix} w \cos(wt) & 0 \\ 0 & -w \cos(wt) \end{pmatrix} \right) = \frac{w \cos(wt)}{2} (\rho_{11} - \rho_{22})$$

It was clear that the heat should come out zero since we are in an isolated system, taking that all the energy is due to work. Using the values obtained earlier for the density components:

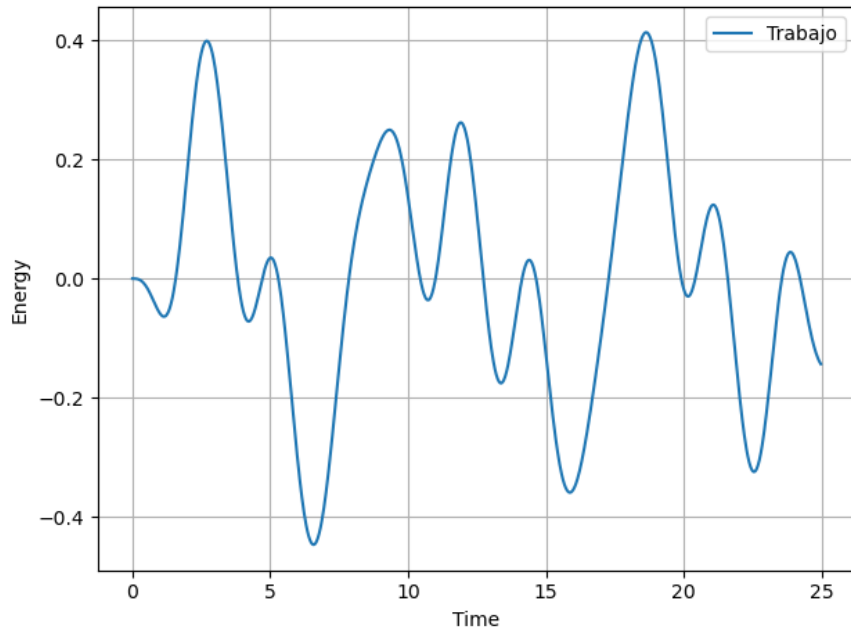
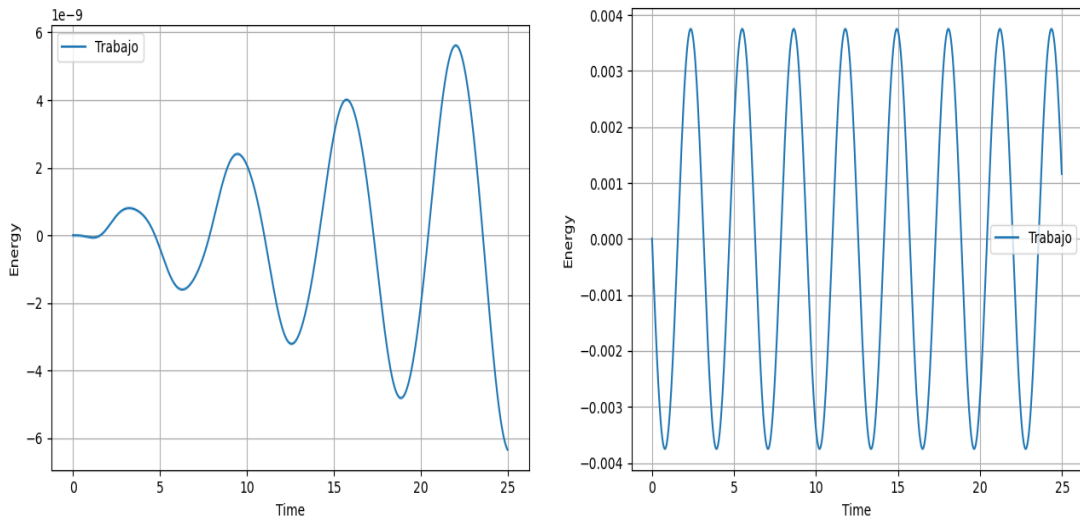


Figure III: Numerical solution of work ($\lambda = \hbar = w = 1$).

As we can observe it's an unpredictable function, it depends to a great extent on the values of the independent term and sinusoidal term. We saw that the heat is zero so we are not going to take it into account for our numerical analysis, all the energy is due to work. Now, there are two borderline cases, in which $\lambda \ll 1$ and in which $\lambda \gg 1$:



(a) Work with $\lambda = 10^{-9}$.

(b) Work with $\lambda = 10^2$.

Figure IV: Work in two borderline cases.

We see that they clearly have two behaviors, in the case of $\lambda = 10^{-9}$ we see a periodic function that grows, however, it oscillates in values very close to 0, tending to a very small value as time progresses as it can be seen in V. This was all to be expected since a very small λ should recover the previous example where the work is zero. On the other hand, we see that the solution for $\lambda = 10^2$ has a sinusoidal form and is not null since the parameter adds work to the system.

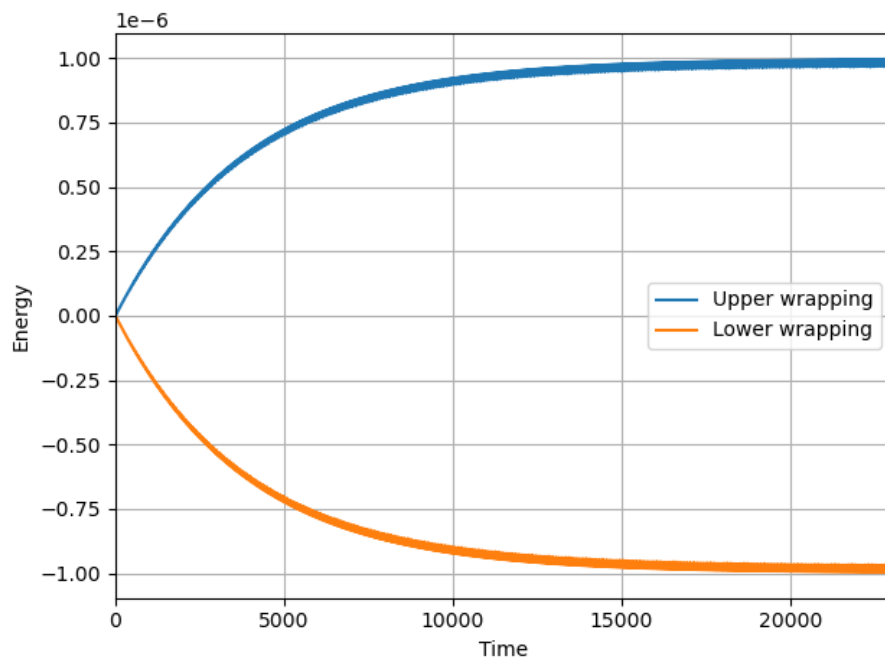


Figure V: Work with $\lambda = 10^{-9}$ for $t \gg 1$.

3 Chapter 2: Definition of work; two-point measurements protocol

Abstract

El objetivo final de este apartado es obtener los distintos valores del trabajo así como su distribución de probabilidad a distintos tiempos. Para ello, primero debemos caracterizar el operador evolución temporal y obtener su forma matricial. Esto se consigue mediante una rotación específica que convierta nuestro hamiltoniano en un hamiltoniano independiente del tiempo, pudiendo así calcular directamente el operador evolución.

Ya con este operador debemos calcular el operador densidad de estados, que va a depender de la temperatura del sistema cuántico en cuestión. Utilizando este a tiempo 0 y el de evolución para obtenerlo en un tiempo arbitrario podemos calcular la energía media inicial y final; y con ello, el trabajo medio.

3.1 Time evolution operator

In this section, we closely follow [11] and we are going to calculate the evolution operator in a specific case to be able to use it later to compute the work. We assume an isolated system without a thermal bath whose Hamiltonian varies in time with the form:

$$H_S = \frac{\hbar\omega}{2}\sigma_z - \frac{\Omega}{2}(\sigma_x \sin(\omega_d t) + \sigma_y \cos(\omega_d t)) \quad (12)$$

As we have mentioned, the system is isolated, so $H = H_S(t)$. Now, we can start with the Schrödinger equation 2. This equation is linear, so its time evolution will be given by the action of a certain time evolution operator $U(t)$, such that $|\psi(t)\rangle = U(t)|\psi(t_0)\rangle$. In this way, we arrive at the following equation:

$$i\hbar \frac{\partial}{\partial t} U(t) = H_S(t)U(t) \quad \text{where } U(0) = \mathbb{1} \quad (13)$$

To deal with our particular case, we are going to assume the form of $U(t)$ depending on a parameter α , in such a way that:

$$U(t) = e^{-\frac{i}{\hbar}\alpha\sigma_z t} \tilde{U}(t) \quad (14)$$

For simplicity in the calculations, the notation $U = U(t)$ and $\tilde{U} = \tilde{U}(t)$ is used. Substituting in 13 and conveniently operating:

$$i\hbar \frac{\partial U}{\partial t} = i\hbar \left(-\frac{i}{\hbar} \alpha \sigma_z e^{-\frac{i}{\hbar} \alpha \sigma_z t} \tilde{U} + e^{-\frac{i}{\hbar} \alpha \sigma_z t} \frac{\partial \tilde{U}}{\partial t} \right) = H_S e^{-\frac{i}{\hbar} \alpha \sigma_z t} \tilde{U}$$

$$\alpha \sigma_z e^{-\frac{i}{\hbar} \alpha \sigma_z t} \tilde{U} + i\hbar e^{-\frac{i}{\hbar} \alpha \sigma_z t} \frac{\partial \tilde{U}}{\partial t} = H_S e^{-\frac{i}{\hbar} \alpha \sigma_z t} \tilde{U}$$

Multiplying by $e^{\frac{i}{\hbar} \alpha \sigma_z t}$ on both sides from the left, knowing that it commutes with σ_z , and simplifying:

$$\alpha \sigma_z \tilde{U} + i\hbar \frac{\partial \tilde{U}}{\partial t} = e^{\frac{i}{\hbar} \alpha \sigma_z t} H_S e^{-\frac{i}{\hbar} \alpha \sigma_z t} \tilde{U}$$

Substituting H_S from the expression 12 and then rearranging terms for simplicity:

$$\alpha \sigma_z \tilde{U} + i\hbar \frac{\partial \tilde{U}}{\partial t} = e^{\frac{i}{\hbar} \alpha \sigma_z t} \left(\frac{\hbar \omega}{2} \sigma_z - \frac{\Omega}{2} (\sigma_x \sin(\omega_d t) + \sigma_y \cos(\omega_d t)) \right) e^{-\frac{i}{\hbar} \alpha \sigma_z t} \tilde{U}$$

Finally:

$$i\hbar \frac{\partial \tilde{U}}{\partial t} = \left(\frac{\hbar \omega}{2} - \alpha \right) \sigma_z \tilde{U} - \frac{\Omega}{2} e^{\frac{i}{\hbar} \alpha \sigma_z t} [\sigma_x \sin(\omega_d t) + \sigma_y \cos(\omega_d t)] e^{-\frac{i}{\hbar} \alpha \sigma_z t} \tilde{U} \quad (15)$$

Now we must calculate the action of the exponentials on the Pauli matrices σ_x and σ_y of the second addend. To do this, we can do a Taylor series expansion of the exponential matrix function for any Pauli matrix σ_n , that is:

$$e^{\frac{i}{\hbar} \alpha \sigma_n t} = \mathbb{1} + i \sigma_n \left(\frac{\alpha t}{\hbar} \right) + \frac{i^2 \sigma_n^2}{2!} \left(\frac{\alpha t}{\hbar} \right)^2 + \frac{i^3 \sigma_n^3}{3!} \left(\frac{\alpha t}{\hbar} \right)^3 + \frac{i^4 \sigma_n^4}{4!} \left(\frac{\alpha t}{\hbar} \right)^4 + \dots$$

Grouping the terms into real and imaginary parts:

$$e^{\frac{i}{\hbar} \alpha \sigma_n t} = \left\{ \mathbb{1} - \frac{\sigma_n^2}{2!} \left(\frac{\alpha t}{\hbar} \right)^2 + \frac{\sigma_n^4}{4!} \left(\frac{\alpha t}{\hbar} \right)^4 + \dots \right\} + i \left\{ \sigma_n \left(\frac{\alpha t}{\hbar} \right) - \frac{\sigma_n^3}{3!} \left(\frac{\alpha t}{\hbar} \right)^3 + \dots \right\}$$

In this way, it is clearly seen that the terms grouped in the real part correspond to an expansion of the cosine function and the terms grouped in the imaginary part to a sinusoidal function. This allows us to rewrite the matrix rotation operator as follows:

$$e^{\frac{i}{\hbar} \alpha \sigma_n t} = \mathbb{1} \cos \left(\frac{\alpha t}{\hbar} \right) + i \sigma_n \sin \left(\frac{\alpha t}{\hbar} \right) \quad (16)$$

A more abstract version of the general 2×2 matrix can be found by applying Sylvester's formula to give a generic 16 version for the analytic function [10].

In our case, $\sigma_n = \sigma_z$ so we can elaborate the following product that appears in the equation 15:

$$e^{\frac{i}{\hbar}\alpha\sigma_z t} [\sigma_x \sin(\omega_d t) + \sigma_y \cos(\omega_d t)] e^{-\frac{i}{\hbar}\alpha\sigma_z t} = \\ = \left(\mathbb{1} \cos\left(\frac{\alpha t}{\hbar}\right) + i\sigma_z \sin\left(\frac{\alpha t}{\hbar}\right) \right) [\sigma_x \sin(\omega_d t) + \sigma_y \cos(\omega_d t)] \left(\mathbb{1} \cos\left(\frac{\alpha t}{\hbar}\right) - i\sigma_z \sin\left(\frac{\alpha t}{\hbar}\right) \right)$$

Doing this product of matrices and applying trigonometric properties we arrive at:

$$\begin{pmatrix} 0 & -i \cos\left(\frac{2\alpha t}{\hbar} + \omega_d t\right) + \sin\left(\frac{2\alpha t}{\hbar} + \omega_d t\right) \\ i \cos\left(\frac{2\alpha t}{\hbar} + \omega_d t\right) + \sin\left(\frac{2\alpha t}{\hbar} + \omega_d t\right) & 0 \end{pmatrix} = \\ = \sin\left(\frac{2\alpha t}{\hbar} + \omega_d t\right) \sigma_x + \cos\left(\frac{2\alpha t}{\hbar} + \omega_d t\right) \sigma_y$$

Now, we can choose α in such a way that the Hamiltonian is not dependent on time. To do this we take out i common factor and convert the interior into an exponential:

$$\begin{pmatrix} 0 & -i (\cos\left(\frac{2\alpha t}{\hbar} + \omega_d t\right) + i \sin\left(\frac{2\alpha t}{\hbar} + \omega_d t\right)) \\ i (\cos\left(\frac{2\alpha t}{\hbar} + \omega_d t\right) - i \sin\left(\frac{2\alpha t}{\hbar} + \omega_d t\right)) & 0 \end{pmatrix} = \\ \begin{pmatrix} 0 & -ie^{i\left(\frac{2\alpha}{\hbar} + \omega_d\right)t} \\ ie^{-i\left(\frac{2\alpha}{\hbar} + \omega_d\right)t} & 0 \end{pmatrix}$$

It is clear that to make the previous expression independent of time it would be necessary to make the exponent null, for this trivially:

$$\alpha = -\frac{\omega_d \hbar}{2} \implies \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad (17)$$

Once we have obtained this addend we can return to 15 to solve the differential equation. However, by obtaining a time-independent Hamiltonian, we can directly calculate the evolution operator by doing the rotation. We find that such Hamiltonian is:

$$\tilde{H} = \frac{\hbar}{2}(\omega + \omega_d)\sigma_z - \frac{\Omega}{2}\sigma_y \quad (18)$$

Now, we can obtain the evolution operator as:

$$U(t) = e^{-\frac{i}{\hbar}\alpha\sigma_z t} e^{-\frac{i}{\hbar}\tilde{H}t} =$$

$$= \begin{pmatrix} e^{i\omega_d t/2} & 0 \\ 0 & e^{-i\omega_d t/2} \end{pmatrix} \left[\begin{pmatrix} e^{-i(\omega_d+\omega)t/2} & 0 \\ 0 & e^{i(\omega_d+\omega)t/2} \end{pmatrix} \begin{pmatrix} \cos\left(\frac{\Omega t}{2\hbar}\right) & \sin\left(\frac{\Omega t}{2\hbar}\right) \\ -\sin\left(\frac{\Omega t}{2\hbar}\right) & \cos\left(\frac{\Omega t}{2\hbar}\right) \end{pmatrix} \right]$$

After operating, and making the product of the matrices, the analytical expression of the evolution operator is finally obtained:

$$U(t) = \begin{pmatrix} \cos\left(\frac{\Omega t}{2\hbar}\right)e^{-\frac{i}{2}\omega t} & \sin\left(\frac{\Omega t}{2\hbar}\right)e^{-\frac{i}{2}\omega t} \\ -\sin\left(\frac{\Omega t}{2\hbar}\right)e^{\frac{i}{2}\omega t} & \cos\left(\frac{\Omega t}{2\hbar}\right)e^{\frac{i}{2}\omega t} \end{pmatrix} \quad (19)$$

Below we represent the form of $u(t)$ and $v(t)$ that we will use in the next section:

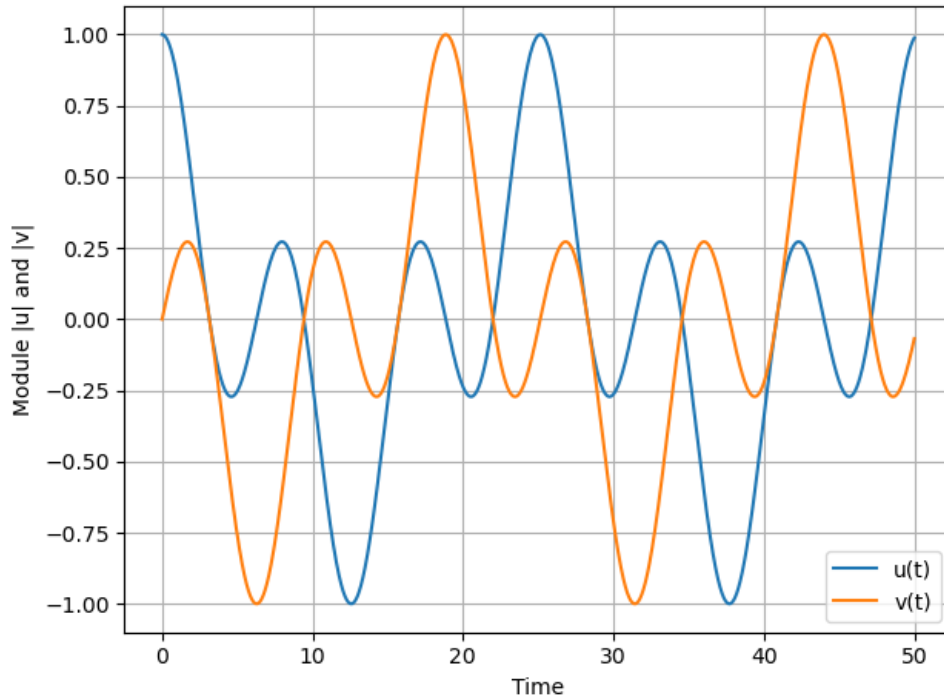


Figure VI: $u(t)$ and $v(t)$ components of evolution operator ($\hbar = \omega = 1, \Omega = 1/2$).

3.2 Definition of $W(t)$

We have a solution for the time-dependent evolution operator which, as expected, has the form:

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

Where $u(t) = \cos\left(\frac{\Omega t}{2\hbar}\right)e^{-\frac{i}{2}\omega t}$ and $v(t) = \sin\left(\frac{\Omega t}{2\hbar}\right)e^{-\frac{i}{2}\omega t}$.

Now with the shape of these functions we can compute the work, for this the first thing would be to define an initial state for the density of states operator [11]:

$$\rho_{th} = Z^{-1}e^{\beta H(0)}$$

Where Z is the canonical partition function $Z = \text{Tr}(e^{-\beta H})$ and $\beta = \frac{1}{K_B T}$. In later calculations, we will assume $K_B = 1$.

From 12 it is clear that $H(t = 0) = \frac{\hbar\omega}{2}\sigma_z - \frac{\Omega}{2}\sigma_y$. However, we are going to assume the case that $\Omega \ll \hbar\omega$, so the canonical partition function remains:

$$Z = \text{Tr}(e^{-\beta H(0)}) = \text{Tr}\left(e^{-\frac{\beta\hbar\omega}{2}\sigma_z}\right) = \text{Tr}\begin{pmatrix} e^{-\frac{\beta\hbar\omega}{2}} & 0 \\ 0 & e^{\frac{\beta\hbar\omega}{2}} \end{pmatrix} = 2 \cosh\left(\frac{\beta\hbar\omega}{2}\right)$$

With this, we obtain the following matrix for the density operator at the initial instant dependent on temperature:

$$\rho_{th}(0) = \frac{1}{2} \begin{pmatrix} 1 + \tanh\left(\frac{\beta\hbar\omega}{2}\right) & 0 \\ 0 & 1 - \tanh\left(\frac{\beta\hbar\omega}{2}\right) \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 + f & 0 \\ 0 & 1 - f \end{pmatrix} \quad (20)$$

On the one hand, it is true that $\text{Tr}(\rho_{th}) = 1$, is a necessary condition since the sum of the probabilities must give 1. On the other hand, it is true that when $T \rightarrow \infty$, it says $\beta \rightarrow 0$, the populations equalize, and that when $T \rightarrow 0$ as $\tanh\left(\frac{\beta\hbar\omega}{2}\right) \rightarrow 1$ then the system tends to its ground state; both results agree with what was theoretically expected.

$$T \rightarrow \infty \implies \rho_{th}(0) \rightarrow \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}$$

$$T \rightarrow 0 \implies \rho_{th}(0) \rightarrow \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$$

Now, we must evolve said operator up to a time t in order to subsequently obtain the energy at that time. To do this, we apply the evolution operator previously calculated as follows:

$$\rho_{th}(t) = U(t)\rho_{th}(0)U^\dagger(t) = \frac{1}{2} \begin{pmatrix} u(t) & v(t) \\ -v^*(t) & u^*(t) \end{pmatrix} \begin{pmatrix} 1 + f & 0 \\ 0 & 1 - f \end{pmatrix} \begin{pmatrix} u^*(t) & -v(t) \\ v^*(t) & u(t) \end{pmatrix}$$

Operating and taking into account that logically $|u(t)|^2 + |v(t)|^2 = 1$ since it is the sum of the probability amplitudes, we obtain:

$$\rho_{th}(t) = \frac{1}{2} \begin{pmatrix} 1 + f(|u(t)|^2 - |v(t)|^2) & -2u(t)v(t)f \\ -2u^*(t)v^*(t)f & 1 - f(|u(t)|^2 - |v(t)|^2) \end{pmatrix} \quad (21)$$

With this result we can obtain a lot of things, in this case, we can use it to calculate the mean value of energy at time 0 ($\langle E_i \rangle$) and at time t ($\langle E_f \rangle$). The mean value of the energy at any time it's the trace of the product of the density matrix at this time times the Hamiltonian (in our case is independent of time). So:

$$\langle E_i \rangle = \text{Tr}(\rho_{th}(0)H_o) = \hbar\omega f = \frac{\hbar\omega}{2} \tanh\left(\frac{\beta\hbar\omega}{2}\right) \quad (22)$$

$$\langle E_f \rangle = \text{Tr}(\rho_{th}(t)H_o) = \frac{\hbar\omega}{2} f(|u(t)|^2 - |v(t)|^2) = \frac{\hbar\omega}{2} \tanh\left(\frac{\beta\hbar\omega}{2}\right) (|u(t)|^2 - |v(t)|^2) \quad (23)$$

Now with the form of energy at initial time and at time t we can obtain the average work done in said period of time. It is notorious that since the final energy is equal to the initial one but multiplied by the factor $(|u(t)|^2 - |v(t)|^2)$ and since these are the probability amplitudes that meet $|u(t)|^2, |v(t)|^2 \leq 1$ then $(|u(t)|^2 - |v(t)|^2) \leq 1$; so work is negative, that is, work is exerted on the system (as initially planned).

Now, if we calculate the work like the difference between the final and initial energy we obtain that:

$$\langle W \rangle = \langle E_f \rangle - \langle E_i \rangle = \frac{\hbar\omega}{2} f(|u(t)|^2 - 1 - |v(t)|^2) = -\hbar\omega f |v(t)|^2$$

Replacing everything and leaving it as a function of temperature and time, furthermore, redefining the work as that exerted on the system, we obtain:

$$\langle W \rangle = \hbar\omega \tanh\left(\frac{\beta\hbar\omega}{2}\right) \sin^2\left(\frac{\Omega}{2\hbar}t\right) \quad (24)$$

The first minimum of this function is trivially in $t = 0$ because it is the initial state. The following minimums are located at $t = \frac{2n\pi\hbar}{\Omega}$ where $n \in \mathbb{N}$. On the other hand, the maximums in time of this function are $t = \frac{n\pi\hbar}{\Omega}$ where $n \in \mathbb{N}$. All of these results are shown in the following figure.

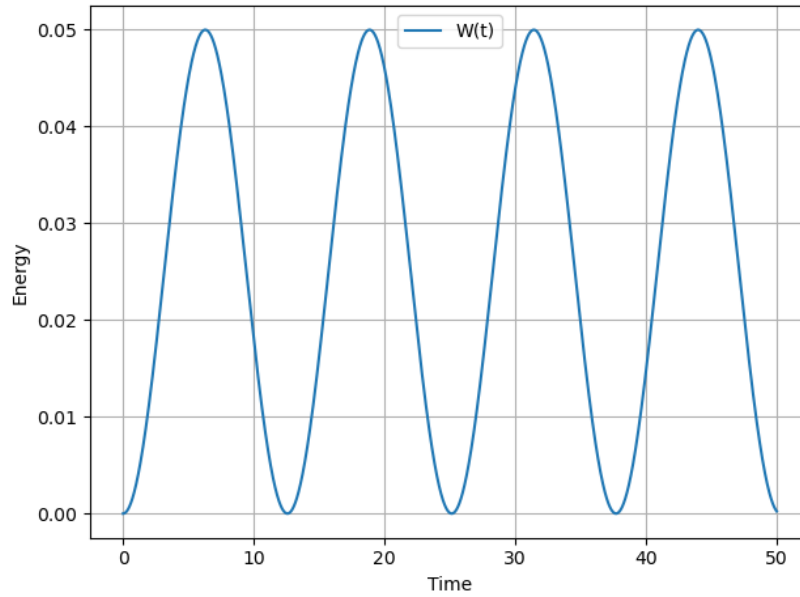


Figure VII: $\langle W \rangle (t)$ ($\hbar = \omega = 1$, $\Omega = 1/2$ and $\beta = 1/10$).

Another fact that we can observe is that as the temperature increases, β decreases, thus decreasing the hyperbolic tangent, that is when $T \rightarrow \infty$ then $\langle W \rangle = 0$. This is coherent if we think that when we increase the temperature a lot, the populations equalize, obtaining a mean value of zero. The opposite occurs if we do $T \rightarrow 0$, doing the average value of the maximum work. All this is represented in the following figure:

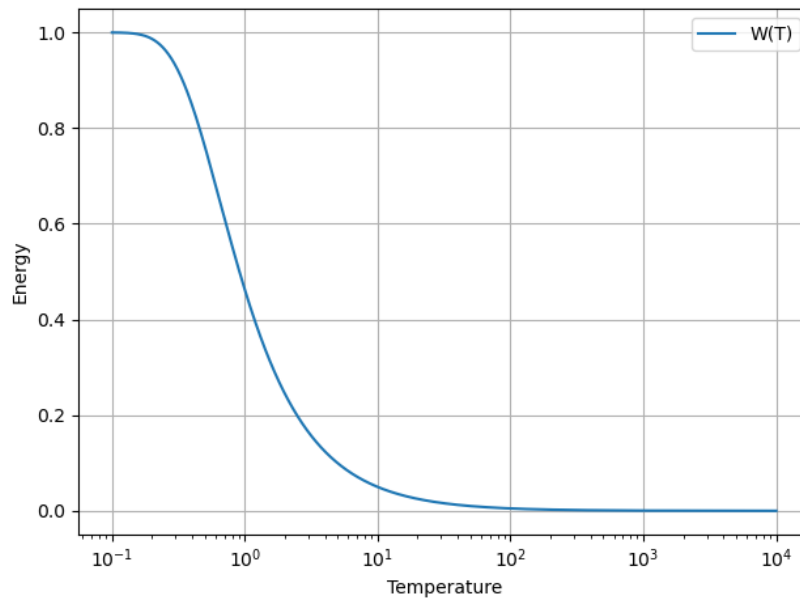


Figure VIII: $\langle W \rangle (T)$ ($\hbar = \omega = 1$, $\Omega = 1/2$ and $t = 2\pi$).

Just because our Hamiltonian is constant ($H_0 \rightarrow H_0$), then in our case $\Delta F = 0$, where F is the Helmholtz Free Energy which is a thermodynamic potential that measures the useful work obtainable from a closed isothermal thermodynamic system. Because of $\langle W \rangle \geq \Delta F$ we expect $\langle W \rangle \geq 0$ as indicated in 24.

In macroscopic systems, the individual measurements are very similar to the average, but in microscopic systems, it doesn't work. We have said before that $\langle W \rangle \geq \Delta F$ but actually, the individual measurements of W can be smaller than ΔF , which leads to local violations of the second law of thermodynamics. Nevertheless, this will not be taken into account for our analysis.

4 Chapter 3: Probability distribution

Abstract

En este capítulo nos adentramos en el cálculo de las probabilidades de obtener los distintos valores posibles del trabajo. Mediante el uso de una simple probabilidad condicionada y definiendo una función característica podemos obtener la distribución de probabilidad completa del trabajo a través de la transformada inversa de Fourier. Posteriormente hemos hecho un análisis estadístico de los resultados de esa transformación. Por otro lado, tras calcularse dicha función característica hemos comprobado si esta cumple la igualdad de Jarzynski haciendo $r = i\beta$ y explicamos sus implicaciones.

Por último hemos analizado qué le ocurre a los valores posibles del trabajo si aumentamos el número de partículas (sin interacción entre sí), obteniendo la distribución de probabilidad para N partículas.

4.1 Work distribution $P(W)$

We will now obtain the probability distribution expression $P(W)$ obtained by repeating the work measurement several times (via the energy in the initial and final states). This can be done bearing in mind that this is a two-point measurement protocol. According to probability theory, if A and B are two events, then the sum of the probabilities $P(A, B)$ of these two events can be written as:

$$P(A, B) = P(A|B)P(B)$$

Where $P(B)$ is the probability that B occurs and $P(A|B)$ is the conditional probability that A occurs if B has occurred. In our context, $P(B)$ are just the initial probabilities P_n and $P(A|B)$ is assigned to the expression:

$$|\langle m|\psi(t)\rangle|^2 = |\langle m|U(t)|n\rangle|^2 \quad (25)$$

That is the probability to measure a final energy E_m^f after a time t after having measured E_n^i and where $|n\rangle$ is the initial state and $|m\rangle$ is the final state. Therefore, the probability that both events occur is:

$$P(E_n^i, E_m^f) = |\langle m|U(t)|n\rangle|^2 P_n \quad (26)$$

Now, since the work is $W = E_m^f - E_n^i$ we can obtain the exact expression of the probability of obtaining the different work values:

$$P(W) = \sum_{n,m} |\langle m|U(t)|n\rangle|^2 P_n \delta(W - (E_m^f - E_n^i)) \quad (27)$$

Where the last term is the Dirac delta function.

Although this equation is correct, it is not practical. Most systems have a large number of allowable energy levels and consequently a large number of allowable energy differences $E_m^f - E_n^i$. It is much more convenient to work with the characteristic function defined by the Fourier transform of the original distribution [11]:

$$G(r) = \langle e^{irW} \rangle = \int_{-\infty}^{\infty} dW P(W) e^{irW} \quad (28)$$

Because $P(W)$ and $G(r)$ are Fourier transforms of each other they have the same information. Besides, we can apply the inverse Fourier transform to obtain the distribution $P(W)$:

$$P(W) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dr G(r) e^{-irW} \quad (29)$$

Starting from the expression 27 and taking into account that our Hamiltonian is constant (H_o) we can arrive at a more convenient expression for $G(r)$:

$$G(r) = \sum_{n,m} |\langle m| U(t) |n\rangle|^2 P_n e^{ir(E_m^f - E_n^i)} = \sum_{n,m} \langle n| U^\dagger(t) e^{irH_o} |m\rangle \langle m| U(t) e^{-irH_o} \rho_{th} |n\rangle$$

Since the definition of the trace is $\text{Tr}(A) := \sum_k \langle A e_k, e_k \rangle$ we obtain the following characteristic function:

$$G(r) = \text{Tr} \left(U^\dagger(t) e^{irH_o} U(t) e^{-irH_o} \rho_{th} \right) \quad (30)$$

This expression has no particularly important physical significance beyond the distribution of work. However, working with $G(r)$ is often much more convenient than $P(W)$ because it is written as a trace of the product of the operators. In many respects, this function plays a role similar to the Z partition function in equilibrium statistical mechanics. Usually, you don't focus on the physical meaning of Z, but use it as a convenient quantity to extract observables like energy and entropy.

So, in our case, we already know all operators because we calculated them before. After computation:

$$\begin{aligned} G(r) &= \text{Tr} \left(\begin{pmatrix} u^*(t) & -v(t) \\ v^*(t) & u(t) \end{pmatrix} \begin{pmatrix} e^{i\frac{\hbar\omega}{2}r} & 0 \\ 0 & e^{-i\frac{\hbar\omega}{2}r} \end{pmatrix} \dots \right) = \dots = \\ &= \frac{1}{2} \text{Tr} \left(\begin{pmatrix} |u(t)|^2 + |v(t)|^2 e^{-i\hbar\omega} & 2iu^*(t)v(t) \sin(\frac{\hbar\omega}{2}r) e^{i\frac{\hbar\omega}{2}r} \\ 2iu(t)v^*(t) \sin(\frac{\hbar\omega}{2}r) e^{-i\frac{\hbar\omega}{2}r} & |u(t)|^2 + |v(t)|^2 e^{i\hbar\omega} \end{pmatrix} \begin{pmatrix} 1+f & 0 \\ 0 & 1-f \end{pmatrix} \right) \end{aligned}$$

Now, doing the last matrix product, calculating the trace and arguing terms we have this expression for their characteristic function:

$$G(r) = |u(t)|^2 + |v(t)|^2 \left(\frac{1+f}{2} e^{-i\hbar\omega r} + \frac{1-f}{2} e^{i\hbar\omega r} \right) \quad (31)$$

With this calculation, we can compute the inverse Fourier transform of the characteristic function to find the probability distribution of employment. Nevertheless, before that, we will introduce the Jarzynski equality since it is an equation of great importance that can be derived from this characteristic function.

[12] Jarzynski equality: Consider a classical system in thermal contact with a heat reservoir at temperature T with some parameters $\vec{\gamma}=(V,B,k,\dots)$. If the parameters of a system change infinitely slowly between two points $\vec{\gamma}_B$ and $\vec{\gamma}_A$ in the parameter space, so that at each moment the system is in thermal equilibrium with the reservoir, then from classical thermodynamics we have that $W = \Delta F$.

Conversely, when a parameter changes in a finite time t_f , the work performed depends on the microscopic initial conditions of the system and reservoir. The fact is that on average the work is more than the free energy change (as obtained in the previous section). In this system, Jarzynski proved that:

$$\langle e^{-\beta W} \rangle = e^{-\beta \Delta F} \quad (32)$$

Based on the definition of the characteristic function if $r = i\beta$ we have that $G(i\beta) = \langle e^{-\beta W} \rangle$. On the other hand, using 30 but with different initial and Hamiltonian state we obtain that:

$$G(i\beta) = \frac{1}{Z_i} \text{Tr} (e^{-\beta H_f}) = \frac{Z_f}{Z_i}$$

The relation between Helmholtz free energy and Z is $F = \frac{1}{\beta} \ln Z$. So, if we substitute that in the last expression we obtain that:

$$G(i\beta) = \frac{e^{-\beta F_f}}{e^{-\beta F_i}} = e^{-\beta \Delta F} = \langle e^{-\beta W} \rangle \quad q.e.d. \quad (33)$$

In our specific case, if we make $r = i\beta$ in the expression 31 we see that the sum inside the parentheses becomes 1 and therefore $G(i\beta) = |u(t)|^2 + |v(t)|^2 = 1$; thus obtaining the Jarzynski equality because, as we saw before, $\Delta F = 0$. We can then conclude that our system satisfies the Jarzynski equality.

At this point, we can go back to the above and calculate the inverse Fourier transform of the characteristic function 29:

$$P(W) = |u(t)|^2 \left(\frac{1}{2\pi} \int_{-\infty}^{\infty} dr e^{-irW} \right) + |v(t)|^2 \frac{1+f}{2} \left(\frac{1}{2\pi} \int_{-\infty}^{\infty} dr e^{-ir(W+\hbar\omega)} \right) + |v(t)|^2 \frac{1-f}{2} \left(\frac{1}{2\pi} \int_{-\infty}^{\infty} dr e^{-ir(W-\hbar\omega)} \right)$$

Taking into account that a Dirac delta can be expressed as $\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dr e^{irx}$ we can simplify the parentheses with the deltas, obtaining:

$$P(W) = |u(t)|^2 \delta(W) + |v(t)|^2 \left(\frac{1+f}{2} \delta(W+\hbar\omega) + \frac{1-f}{2} \delta(W-\hbar\omega) \right) \quad (34)$$

From this expression, we can distinguish 3 different values for the work $W \in \{-\hbar\omega, 0, \hbar\omega\}$ that corresponds to a "photon absorption", no change, and a "photon emission" respectively. Something important to note is that we only obtain 3 values due to the approximation taken before ($\Omega \ll \hbar\omega$), if we had not taken this approximation we would have more possible combinations for the work.

All these possibilities appear next to their probability amplitudes. This can be easily verified if, for example, we see that the initial probability of absorbing a photon is $\frac{1-f}{2}$ and taking into account the transition probability $|\langle - | U(t) | + \rangle|^2 = |v(t)|^2$ we obtain $P(W = -\hbar\omega) = \frac{1-f}{2} |v(t)|^2$, which is what accompanies to the delta of said value. This reasoning can be replicated with the rest of the values, obtaining said amplitudes.

$$P(W = -\hbar\omega) = \frac{1-f}{2} |v(t)|^2 \quad (35)$$

$$P(W = 0) = |u(t)|^2 \quad (36)$$

$$P(W = \hbar\omega) = \frac{1+f}{2} |v(t)|^2 \quad (37)$$

An important conclusion to highlight is that the probability of emitting a photon is not the same as that of absorbing it, which makes sense with the previous results, since otherwise the average work would be zero. In fact as $f = \tanh\left(\frac{\beta\hbar\omega}{2}\right)$ and in general $\frac{\beta\hbar\omega}{2} \geq 0$ then $\tanh\left(\frac{\beta\hbar\omega}{2}\right) \geq 0$ so $1+f \geq 1-f$. This means that the probability of absorbing a photon is less than that of emitting it, that is, $P(W = \hbar\omega) \geq P(W = -\hbar\omega)$ thus leading to the mean value of the work being greater than 0 even though there may be local violations of the second law.

Also, we can calculate the relation between the probability of absorption and emission:

$$\frac{P(W = -\hbar\omega)}{P(W = \hbar\omega)} = \frac{1 - f}{1 + f} = \frac{1 - \tanh\left(\frac{\beta\hbar\omega}{2}\right)}{1 + \tanh\left(\frac{\beta\hbar\omega}{2}\right)} = \frac{\cosh\left(\frac{\beta\hbar\omega}{2}\right) - \sinh\left(\frac{\beta\hbar\omega}{2}\right)}{\cosh\left(\frac{\beta\hbar\omega}{2}\right) + \sinh\left(\frac{\beta\hbar\omega}{2}\right)}$$

Using the properties $\cosh x + \sinh x = e^x$ and $\cosh x - \sinh x = e^{-x}$ we conclude that:

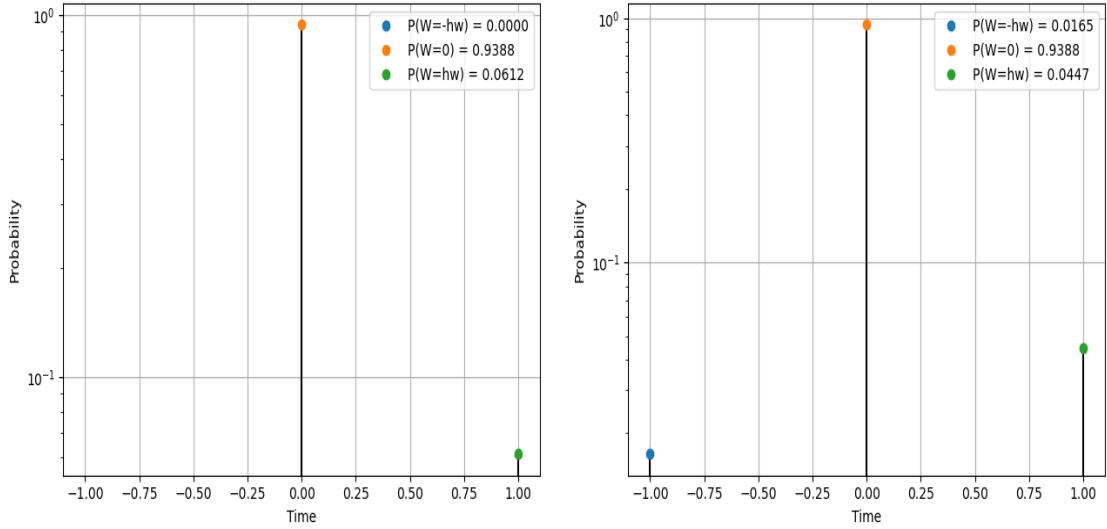
$$\frac{P(W = -\hbar\omega)}{P(W = \hbar\omega)} = e^{-\beta\hbar\omega} \quad (38)$$

That satisfies the detailed balance principle [13], which is used in kinetic systems which are decomposed into elementary processes like collisions.

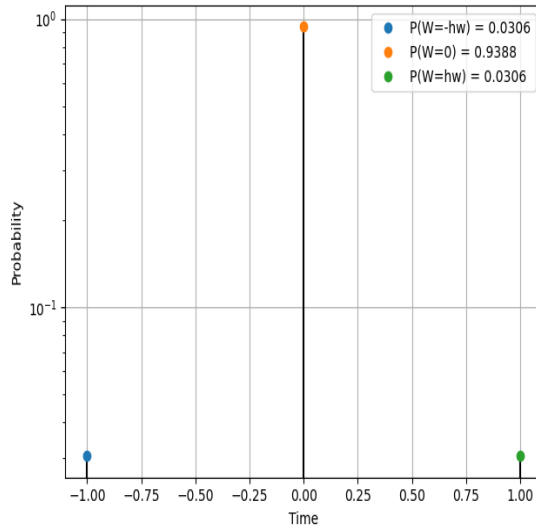
Now, we can compute also how the probability distribution varies in function of temperature T . Since temperature affects populations, it is to be expected that it will affect the probabilities of obtaining one or the other value for work.

As expected, we can see 3 facts in figure IX:

- 1. When $T \rightarrow 0$, that is, $\beta \rightarrow \infty$ the probability $P(W = \hbar\omega)$ absorbs all the probability of $P(W = -\hbar\omega)$. This is because, at low temperatures, the system tends to the ground state as we saw before.
- 2. The probability $P(W = 0)$ does not vary with temperature.
- 3. When $T \rightarrow \infty$, that is, $\beta \rightarrow 0$ the probabilities $P(W = \hbar\omega)$ and $P(W = -\hbar\omega)$ are equal. This is due to the fact that, as we mentioned before, with the increase in temperature the populations in the fundamental and excited states are equalized.



(a) Probability distribution with $\beta = 10^3$. (b) Probability distribution with $\beta = 1$.



(c) Probability distribution with $\beta = 10^{-3}$.

Figure IX: Probability distribution $P(W)$ borderline cases ($\hbar = \omega = 1, \Omega = 1/2$).

Another statistical data that we can compute thanks to the characteristic function is the variance. To do this, knowing that this function can be expressed as the following exponential, we can do an expansion in the Taylor series:

$$G(r) = \langle e^{irW} \rangle = 1 + ir \langle W \rangle - \frac{r^2}{2!} \langle W^2 \rangle + \dots \quad (39)$$

Doing this expansion to the result obtained 31 we obtain that the second order term remains $\langle W^2 \rangle = \hbar^2 \omega^2 |v(t)|^2$. Having this, we can now compute the variance as:

$$\sigma^2(W) = \langle W^2 \rangle - \langle W \rangle^2 = \hbar^2 \omega^2 |v(t)|^2 (1 - f^2 |v(t)|^2) \quad (40)$$

As $f = \tanh \frac{\beta \hbar \omega}{2}$ and $\beta = 1/T$ as the temperature increases the dispersion in the work data increases, obtaining the maximum variance when $T \rightarrow \infty$ being $\sigma_{max}^2(W) = \hbar^2 \omega^2 |v(t)|^2$. The minimum in the variance will then be obtained when $T \rightarrow 0$ being $\sigma_{min}^2 = \hbar^2 \omega^2 |v(t)|^2 (1 - |v(t)|^2)$.

4.2 Work distribution on a large number of particles

So far we have analyzed only one particle system. However, in most situations, it is still common to deal with systems containing a large number of particles. Therefore, the next step is to consider the work done on N particles. For simplicity, we assume that the particles do not interact.

Work is the difference in energy, and for non-interacting systems, energy is an additive quantity. Therefore, the total work W_T done in a particular process is the total work done on each particle:

$$W_T = W_1 + W_2 + \dots + W_N \quad (41)$$

Since the particles do not interact, they will absorb or emit photons whether other particles interact or not; this means that the average work of N particles will be N times the average work of one particle. If we go back to the definition of the characteristic function 30 and take into account that each individual particle is going to have the same function, we get:

$$G_T(r) = \langle e^{irW_T} \rangle = \langle e^{irW_1} \rangle \dots \langle e^{irW_N} \rangle = G(r)^N = (\alpha + \gamma_+ e^{-i\hbar\omega r} + \gamma_- e^{i\hbar\omega r})^N \quad (42)$$

Where $\alpha = |u(t)|^2$ and $\gamma_{\pm} = |v(t)|^2 \frac{1 \pm f}{2}$.

This is a trinomial expansion and we can calculate it as:

$$(a + b + c)^n = \sum_{\substack{i,j,k \\ i+j+k=n}} \binom{n}{i,j,k} a^i b^j c^k \quad (43)$$

Where $\binom{n}{i,j,k} = \frac{n!}{i!j!k!}$; $n = N$; $a = \alpha$; $b = \gamma_+ e^{-i\hbar\omega r}$ and $c = \gamma_- e^{i\hbar\omega r}$.

Taking into account that the combinatorial numbers that will appear are only coefficients, like α and γ_{\pm} , we could rewrite the interior of the summation as $C_{k-j} e^{i\hbar\omega r(k-j)}$, where if we do $m = k - j$ (that means we can have values from -N to +N) we finally obtain:

$$G_T(r) = \sum_{m=-N}^N C_m e^{i\hbar\omega r m} \quad (44)$$

Now if we perform the inverse Fourier transform as we did in the previous section, we get a sum of exponential integrals similar to the previous section. This means we will have the sum of the Dirac deltas as possible values of the work:

$$P(W_T) = \sum_{m=-N}^N C_m \delta(W_T - m\hbar\omega) \quad (45)$$

This means that in a system of N particles that do not interact with each other, there will be $2N+1$ possible values for work (since we include the possibility of no work). This makes sense if you think of a single system, since it has 3 possible energy values (fulfills the $2N+1$ values) and you measure work by measuring the energy in two steps, where possible energies are $\frac{\hbar\omega}{2}$ and $-\frac{\hbar\omega}{2}$, and thus possible combinations would be $-\hbar\omega$, 0 and $\hbar\omega$. It is reasonable to think that in a system of N non-interacting particles, this is reproduced, yielding $2N+1$ combinations when measuring the initial and then final energies.

5 Conclusions

The first thing we can conclude is that, as we saw in Chapter 1, despite having a classical definition, work, and heat can also find quantum counterparts, such as the trace of the product of two operators 5 and 6. We have seen two examples, in which thanks to applying equations such as 4 we have been able to obtain the average work dependent on time.

Something important to note is that although we can define the work thanks to operators, this is not an operator. The easiest way to see this is if we use the two-point measurement protocol described in Chapter 2. This leads us to the fact that the work is $W = E_m^f - E_n^i$ which means that the number of possible values is greater than the dimension of the Hilbert space of the Hamiltonian, concluding that the work is not an observable and, in fact, it characterizes a process and not a state.

On the other hand, we have seen throughout Chapter 2 that the use of the time evolution operator can greatly simplify the calculations for mean work. We have seen that the density matrix tends to have equality between populations at very high temperatures and tends to the ground state at very low temperatures. The latter will affect the dependence on the average working temperature, being maximum at low temperatures and minimum at high temperatures. Regarding temporal dependence, it is clear that this is going to be a cyclical process, varying

in this case in the form of $\sin^2(x)$, that is, it will always be positive and greater than the variation of the Helmholtz free energy.

Finally, in Chapter 3 we have seen that defining a characteristic function that is the Fourier transform of the probability distribution can help to easily obtain the work distribution. Once obtained, it is easy to show that it meets the Jarzynski equality as well as the possible values and their probability amplitudes, finding an equilibrium that helps explain why the mean value of energy is positive and seeing that populations behave with temperature, same as mentioned above. This method is so powerful that it can even help us to obtain the probability distribution of a system with N non-interacting particles, obtaining $2N+1$ possible values for the work.

To conclude, in this project what was expected has been achieved: to study and understand a quantum extension of the classical notion work and being able to compute it in different ways. In the process, we have achieved results that are consistent with the theory and physics we know. A possible way to complete it is to submit the system to a thermal bath, studying the heat and how this affects the work and its distribution, that is certainly of reach at the undergraduate level.

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6 Anexo

Code example of Runge Kutta Orden 4:

```

#Importamos los paquetes
import numpy as np
import matplotlib.pyplot as plt
import math

#Le damos un valor a las variables
w = 1
l = 1
#Definimos las ecuaciones diferenciales a tratar
def F(t,X):
    M = np.array([[0, 1j*1/2, -1j*1/2, 0 ], [1j*1/2, -1j*3*np.sin(w*t)/2,
    0, -1j*1/2], [-1j*1/2, 0, 1j*3*np.sin(w*t)/2, 1j*1/2], [0, -1j*1/2,
    1j*1/2, 0 ]])
    X = np.array(X)
    return M@X

#Creamos la función de Runge Kutta por pasos
def runge_kutta4(F,h,n,X0,t0):
    X = [None]*n
    X[0] = np.array(X0)
    global T
    T = [t0+i*h for i in range(n)]
    for i in range(n-1):
        K1 = h*F(T[i],X[i])
        K2 = h*F(T[i]+h/2, X[i]+K1/2)
        K3 = h*F(T[i]+h/2, X[i]+K2/2)
        K4 =h*F(T[i]+h/2, X[i]+K3)
        X[i+1] = X[i] + (K1+2*K2+2*K3+K4)/6
    return X

#Añadimos el tamaño, el número de y evaluamos la función con ciertas
#condiciones iniciales
XNum = runge_kutta4(F, 0.025, 1000, [0.5,-0.5,-0.5,0.5], 0)

#Separamos las variables que queremos obtener de la matriz resultante
Rho11 = [XNum[i][0] for i in range(len(XNum))]
Rho12 = [XNum[i][1] for i in range(len(XNum))]
Rho21 = [XNum[i][2] for i in range(len(XNum))]
Rho22 = [XNum[i][3] for i in range(len(XNum))]

```

Wrapping of a function:

```

def encontrar_minimos_maximos(array):
    minimos = []
    maximos = []

    # Comprobamos si el primer elemento es mínimo o máximo
    if array[0] < array[1]:
        minimos.append(array[0])
    else:
        maximos.append(array[0])

    # Comprobamos los elementos intermedios
    for i in range(1, len(array) - 1):
        if array[i] < array[i - 1] and array[i] < array[i + 1]:
            minimos.append(array[i])
        elif array[i] > array[i - 1] and array[i] > array[i + 1]:
            maximos.append(array[i])

    # Comprobamos si el último elemento es mínimo o máximo
    if array[-1] < array[-2]:
        minimos.append(array[-1])
    else:
        maximos.append(array[-1])

    return minimos, maximos

minimos,maximos = encontrar_minimos_maximos(W(t)) #W(t) es la función que
#tenía definida, solo haría falta cambiarlo por la función de la que
#pintamos la envolvente
  
```