FOUNDATIONS AND APPLICATIONS OF QUANTUM THERMODYNAMICS:

COUPLED DOUBLE QUANTUM DOTS HEAT ENGINES

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The members of the Committee appointed to examine the dissertation of JEFFERSON LUAN DINIZ DE OLIVEIRA find it satisfactory and recommend that it be accepted.

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Abstract

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Quantum thermodynamics is an emergent theory in physics that investigates thermodynamic properties of small systems where the quantum effects become relevant. This study relies upon the proposal of a conceptual design for a quantum thermal machine using a model of coupled double quantum dots (DQDs), each DQD with an excess electron to interact, as the working medium.

A general review on the foundations of classical and quantum thermodynamics is provided as well as the characterization of the quantum dots used in the proposed heat engine. The machine operates as an Otto engine in equilibrium conditions; our analysis shows the appearance of different regimes of operations as we adjust external parameters. These operation modes being the heater, the heat engine, or the refrigerator can also be alternated when considering the effects due to the *quantum tunneling* of a single electron between each quantum dot in the DQDs.

Keywords: Quantum Thermodynamics, Quantum Thermal Machines, Coupled Double Quantum Dots, Double Quantum Dots, Quantum Dots.

Resumo

Termodinâmica Quântica é uma teoria emergente na física que investiga as propriedades termodinâmicas de sistemas pequenos onde efeitos quânticos se tornam relevantes. Este estudo se baseia na proposta de uma máquina térmica quântica usando um modelo de pontos quânticos duplos acoplados, cada ponto quântico duplo com um elétron excedente para interagir, como a substância de trabalho.

Uma revisão geral dos fundamentos da termodinâmica clássica e quântica é fornecida, assim como a caracterização dos pontos quânticos usados na máquina térmica proposta. A máquina opera como um motor de Otto em condições de equilíbrio; nossa análise mostra o surgimento de diferentes regimes de operações à medida que ajustamos parâmetros externos. Esses modos de operação sendo o aquecedor, o motor térmico, ou o refrigerador também podem ser alternados ao considerar os efeitos devido ao tunelamento quântico de um único elétron entre cada ponto quântico nos pontos quânticos duplos.

Palavras-chave: Termodinãmica Quântica, Máquinas Térmicas Quânticas, Pontos Quânticos Duplos Acoplados, Pontos Quânticos Duplos, Pontos Quânticos.

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INTRODUCTION

Thermodynamics emerged in the 19th century as a necessity of the Industrial Revolution, where thermal machines were widely manufactured and used with almost no formal theoretical knowledge about them. Thermodynamics focused on the macroscopic properties of the systems and the complexity behind its microscopic details was avoided for a long time; even when the microscopic behavior of the system became relevant, it was taken into account as an average over the large number of elements that composed the system. Thermodynamics also played an important role in the history of science by bringing up the famous problem that would later motivate the emergence of a whole new branch in physics. Quantum mechanics was conceived from a thermodynamic inconsistency in the frequency distribution law of black body radiation, where Planck, in 1900, as an act of despair, imposed a restriction to the frequency of the emitted black body radiation.

Being the thermodynamics valid for large-scale macroscopic processes, we may ask ourselves how far down can we go to rescale our system to still be able to study its thermodynamics properties? The study of thermodynamics on this scale only became more urgent at the end of the 20th century, when the experimental manipulation of systems composed of a small number of atoms and ions became possible [1]. In 1959, a seminal paper by Scovil and Schulz-DuBois demonstrated an equivalence between three-level masers and heat engines, where the discrete energy levels of the particles' internal energy lead to the first successful thermodynamic approach for a quantum system [2]. This paper is considered a milestone that started the field of *quantum thermodynamics* [3–5].

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Thermodynamics and quantum mechanics, at first sight, may be regarded as two distinct theories that cannot communicate with each other. The theory of thermodynamics always intended to be applied to macroscopic systems while quantum mechanics introduced itself as an essential theory for the study of microscopic systems, although it is also applicable at any scale. Quantum thermodynamics arose to establish this connection between thermodynamics and quantum mechanics, thus enabling the study of thermodynamic processes on a smaller scale.

In this dissertation we will present a review on quantum thermodynamics partially focused on the many faces of the laws of quantum thermodynamics [3, 4, 6–10]; we will answer how we can establish the laws of thermodynamics for small systems where the quantum effects start to be relevant. The description of quantum thermal machines will also be presented; we will answer how these thermal machines can be described in the quasistatic limit [11, 12] and if one considers far from equilibrium conditions [13–15]. There are few revision topics in quantum thermodynamics [4, 5, 13, 16, 17] and the following review comes to add a different point of view in the literature using some recent results.

Within the context of mesoscopic systems [18], over the past few years, there has been great interest in the study of quantum dots in different aspects, like their optical and electronic properties in the production of displays and photovoltaic devices or the context of quantum information processing [19–21]. A quantum dot is a semiconductor particle and it is sometimes called an *artificial atom* because of its similarities with a real one. The differences between them are their size (at least three orders of magnitude greater than an atom), their shape, and the strength of the confining potential. Double quantum dots are, as the name suggests, two quantum dots coupled in series [22, 23]. Then, it is straightforward to understand why they are sometimes called *artificial molecules*. Following this reasoning, we chose to use a model of quantum dots as the working medium for a proposal of a quantum thermal engine; to be more specific, a system of coupled double quantum dots [24–27] is used, where this coupling corresponds to a Coulomb interaction between electrons inside the

double quantum dots. The calculations and results behind the proposal of this thermal machine are the main goals of this dissertation which brings original content that is organized in a paper accepted for publication in the journal Physical Review E.

Structure of the dissertation

This dissertation is divided into four chapters as follows:

- Chapter 1 introduces a theoretical background that is required for the comprehension of the following chapters. We start with a general description of thermodynamics, with an emphasis in the laws of thermodynamics and the construction of thermal machines. An overview of statistical mechanics is also provided where we will pay special attention to its postulates in the foundations of classical and quantum statistical mechanics.

- Chapter 2 brings the recent connection between thermodynamics and quantum mechanics in the generalized theory of quantum thermodynamics. The role of the laws of thermodynamics in the quantum realm will be explored together with the description of the quantum thermal machines.

- Chapter 3 gives a short introduction to the study of the quantum dots. The comprehension of the quantum dots is necessary to the application in the original results obtained in this dissertation summarized in chapter 4.

- Chapter 4 reports the original results obtained in this dissertation. Using a system of coupled double quantum dots as the working medium, a quantum thermal machine is proposed and a detailed description of the operation of the machine will be provided.

Chapter One

Thermodynamics and Statistical Mechanics

In this chapter, we introduce all the basic background concepts necessary to the development of the following chapters. We start with a short review on classical thermodynamics, we talk about the laws of thermodynamics and we classify the most important thermal machines operating in finite and infinite time. Next, we introduce also a short review of the main ideas behind the theory of classical and quantum statistical mechanics, its postulates, and the characterization of the ensembles. Finally, we discuss the validity of the foundations of statistical mechanics and present alternative ways of constructing the statistical mechanics without the postulate of equal a priori probability.

1.1   Thermodynamics

" [Thermodynamics is] the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown". These are precisely the words of the most famous physicist of the twentieth century. Even for a genius as Einstein, misconceptions can be said and he really did it so many times, but, as far as we know, this is not the case. The laws of thermodynamics

have never been overthrown by any experiment since its first formulations in the 19th century, at least not in the realm of applicability they always humbly intended to be valid.

Unlike other physical theories, like classical mechanics, electromagnetism, or even quantum mechanics, thermodynamics did not start within a reductionist view of the world, it did not start with a description of a few particles[1] for then to generalize it, it does not try to explain the macro from the micro, it already has been formulated in the limit of many particles, and by many, I mean a huge number of particles (something like $\sim 10^{23}$ particles, or even more).

When the English physicist James Joule performed his famous experiment in 1845, he discovered not only that heat is a form of energy, and consequently, it could be transformed into other forms of energy, but he was also the first one to show that energy has a physical meaning, it is not just a mathematical concept invented by the physicists. Its experiment consists of paddles immersed in water mounted on a vertical shaft and rotated by a cord propelled by falling weights, as illustrated in figure 1.1. As the weights are released, the paddles start to rotate and generates motion in the water, this motion, Joule observed, causes an increase in the temperature of the water, in other words, the gravitational potential energy of the weights are converted into kinetic energy of the paddles, which in turn are converted into heat that causes an increase in the internal energy of the water. Therefore, this proves that heat is not a fluid that flows from warm bodies to cold ones, as it was thought in the past, but it is a form of energy and we can measure it as a physical quantity. Thus, adding this result with the principle of conservation of energy, the first law of thermodynamics could then be formulated: for a process in a defined system, the change in internal energy ΔU is equal to the amount of heat absorbed Q minus the work done W,

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

[1]Only in the 19th century, the Hungary-American mathematician, John von Neumann formulated the concept of temperature for a single particle.
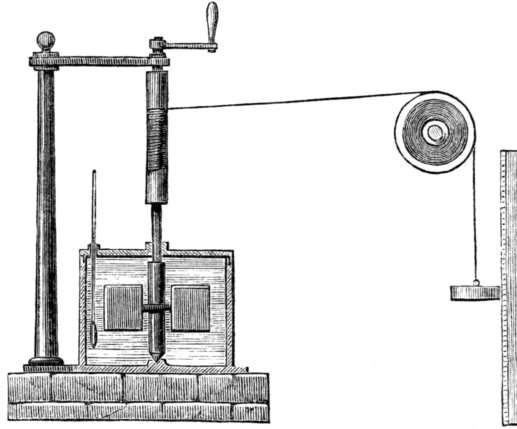
Figure 1.1 Joule's apparatus for measuring the mechanical equivalent of heat.

Now, let us asks ourselves the following about Joule's experiment, the first law of thermodynamics states that it would be possible to spontaneously cool the water and use this energy to pull the weights up, why this will never occur? There is no violation of the conservation of energy in the process described above, but something as fundamental as it is being transgressed, the second law of thermodynamics. This law was first addressed in 1824 by the French engineer Nicolas Sadi Carnot, but it was just precisely enunciated later in 1850 by Rudolf Clausius and, independently, by Lord Kelvin in 1851. Their formulations for the second law of thermodynamics are enunciated as follows:

(**C**): Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time.

(**K**): It is impossible to convert the heat from a single source into work without any other effect.

The Clausius statement (C) forbids the existence of a "miraculous refrigerator" where a machine could remove heat from a colder reservoir into a hotter reservoir at no cost of work, whereas the Kelvin statement (K) forbid the existence of a "miraculous engine", where a machine could remove heat from a reservoir and convert it entirely into work. Despite (C) and (K) seems to state different things, they are equivalent statements. Note that these formulations are entirely based on thermal machines, this is no accident, the 19th century

was marked by the development of these thermal machines during the so-called Industrial Revolution. In the next section, we will be working out these thermal machines explicitly.

1.1.1 Thermal machines

A thermal machine is a device that converts heat into work through a generic *working substance*, an example is the workhorse of the Industrial Revolution, the steam engine, where the working substance for this case is water. From (K) statement, it is clear that a single reservoir is not sufficient to extract heat and produce work *cyclically* (condition required for a machine to continuously operate), so we need two reservoirs at different temperatures[2] $T_h > T_c$, where we define T_h as the temperature of the hotter reservoir and T_c as the temperature of the colder reservoir.

Let Q_h (Q_c) denote the heat transferred between the hot (cold) reservoir and the working substance. The engine must operate cyclically, so there is no variation on the internal energy of the system ($\Delta U = 0$) at the end of each cycle because the system must return to the same initial state, where the system here is the working substance. From equation (1.1), the total work done by the machine W is given by

$$W = Q_h + Q_c. \tag{1.2}$$

Here we have some divergences in the literature about the convention taken to denote the sign of the heat transferred Q and the work done W, no one is right or wrong, it is only notation's complications. Apart from that, we will denote here $Q > 0$ when heat comes from the thermal reservoirs into the system and we denote $W > 0$ when work is done by the machine. Hereupon, we can note that if $Q_h > 0$ and $Q_c < 0$ in equation (1.2), then $W > 0$ if, and only if, $|Q_h| > |Q_c|$, which makes sense because for the machine perform work, we

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[2]Even before Kelvin establish the second law of thermodynamics, this was a requirement already empirically known, remember, there were already existing thermal machines before the whole theory of thermodynamics was formulated.

need more heat entering the system than leaving it, our notation is quite consistent.

An important quantity associated with the heat engine is the measurement of productivity of our engine, how efficiently this engine is converting heat into work. This quantity is called the *efficiency* of the engine and it is defined as the ratio between the work W delivered and the energy Q_h, in form of heat, consumed by the machine to operate

$$\eta = \frac{W}{Q_h} = \frac{Q_h + Q_c}{Q_h} = 1 + \frac{Q_c}{Q_h}, \tag{1.3}$$

where we have used equation (1.2) for the work done. The heat Q_c is a necessary subproduct unreclaimed due to the second law of thermodynamics.

On the other hand, we can have a machine that operates reversely, extracting heat $Q_c > 0$ from the cold reservoir at cost of some work $W < 0$ and exhausting heat $Q_h < 0$ into the hot reservoir. We call this machine a *refrigerator*. We can also measure how efficient this machine is by calculating the ratio of the heat released from the cold heat bath Q_c and the modulus of the total work consumed W in the cycle

$$\varepsilon_R = \frac{Q_c}{|W|} = \frac{Q_c}{-Q_h - Q_c} = \frac{-Q_c}{Q_h + Q_c}, \tag{1.4}$$

where we again have used equation (1.2), remember that $|x| = -x$ if $x < 0$. We call this quantity ε_R the Coefficient of Performance (COP) of the refrigerator.

There is also a third possible machine to work out, the *heat pump*. In this machine we have heat $Q_h > 0$ flowing from the hot reservoir and, at cost of some work $W < 0$, releasing a quantity $Q_c < 0$ into the cold reservoir. We can also define a Coefficient of Performance ε_H for this heat pump as the following

$$\varepsilon_H = \frac{Q_h}{|W|} = \frac{Q_h}{-Q_h - Q_c} = \frac{-Q_h}{Q_h + Q_c}. \tag{1.5}$$

Carnot Cycle

Even though there were already existing thermal machines, only in 1824 with the pioneering work of the French mechanical engineer Nicolas Léonard Sadi Carnot, that was

established the first thermodynamic model of a heat engine. Carnot engine consists of four strokes of ideal thermodynamical processes, and by ideal, I mean a quasistatic process, which is a process that occurs slowly enough for the system to changes its state without losing its thermodynamical equilibrium condition at any time. This could take an infinite time to be plausible, but we are idealizing this machine, we are not worried about constructing it as a physical archetype. These ideal processes are important due to the purpose of the Carnot engine, Carnot idealized a machine that would have the higher efficiency than any other machine operating at the same heat reservoirs, for this we could not have any kind of friction, because friction is directly related to waste and its machine could not tolerate that. Thus we need *isothermal* processes to exchange heat with the heat reservoirs without changing the temperature of the working substance, and *adiabatic* processes to change the temperatures of the working substance during the cycle without heat exchange because we want to avoid the friction associated with the heat conduction.

We have then the following scenario guided by the Pressure-Volume diagram in figure 1.2: (1: a→b) We first have an isothermal expansion from point a to b where the system is put in contact with the hot reservoir at temperature T_h and some heat Q_h is absorbed by the system. (2: b→c) Then the system is separated from the reservoir and undergoes an adiabatic expansion from point b to c decreasing its temperature from T_h to T_c. (3: c→d) From this point on, the system is put in contact with the cold reservoir at temperature T_c and undergoes an isothermal compression from point c to d, where some heat Q_c is released into the reservoir. (4: d→a) Lastly, we have an adiabatic compression from point d to a, where the system is disconnected from the reservoir and starts to increase its temperature from T_c to T_h. This closes the cycle and we could start from (1) again repeating the very same steps. The efficiency η_C of the Carnot engine can be proven to be[3]

$$\eta_C = 1 - \frac{T_c}{T_h}. \tag{1.6}$$

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[3]This is not a difficult task to be done, but it will be easier to prove after we define the concept of entropy.
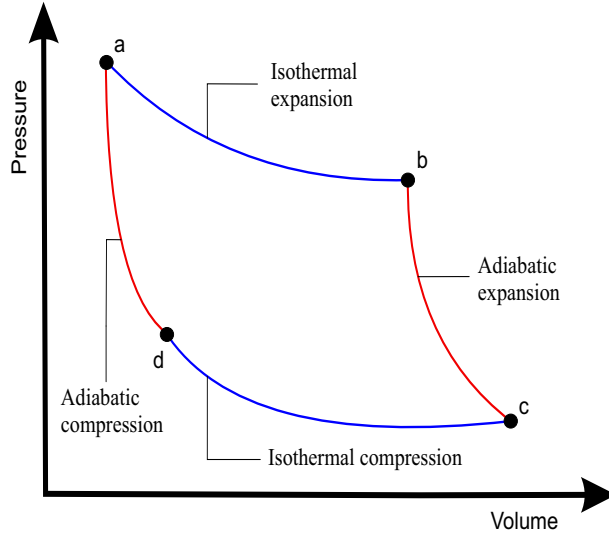
Figure 1.2 Pressure-Volume diagram of a Carnot cycle.

This is the upper limit for the efficiency of any engine operating at the same heat reservoirs T_h and T_c. The frictionless requirement of the Carnot cycle implies that this whole cycle is reversible and we can also have a Carnot refrigerator in which we can establish an upper limit $\varepsilon_C = \frac{1}{T_h/T_c - 1}$ for the COP of any refrigerator, again, operating at the same heat reservoirs T_h and T_c.

Practically all thermal machines rely on, and this is important to emphasize, the *compressibility* of the working substance[4], and on the fact that a hot expansion produces more work than the work required for a cold compression.

Otto Cycle

Even though the patent for the four-stroke engine was acquired in 1861 with the French engineer Alphonse Beau de Rochas, only in 1876 with the German engineer Nicolaus Otto that the spark-ignition engine was first built. This engine is probably the most popular realizable thermal machine, it has been largely applied in many systems throughout history

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[4]Thermoelectric devices being an exception because they are based on the Peltier-Seebeck and Thomson effects, where there is a direct conversion of heat to electric voltage and vice versa. The reader interested in these effects is recommended to take a look in the Ref.[28]

and it is still used nowadays in many cars, small planes, and also small power systems.

The Otto cycle is similar to the Carnot cycle, but instead of the isothermal processes, it has isochoric processes, which are processes where heat can be exchanged with the environment (the reservoirs) but no variation in the volume of the system (the working substance) is allowed. Thus, we have four strokes: (1) An adiabatic compression where the volume of the system decreases from V_h to V_c. (2) An isochoric heat transfer from the cold reservoir to the working substance. (3) An adiabatic expansion where the volume of the system increases from V_c to V_h. (4) An isochoric heat transfer from the hot reservoir to the working substance.

The efficiency η_O of the Otto engine can be proven to be

$$\eta_O = 1 - \frac{1}{r^{\gamma-1}}, \tag{1.7}$$

where $r = V_h/V_c$ is the compression ratio and $\gamma = C_p/C_v$ is the specific-heat ratio of the working substance. The specific heat at constant pressure C_p or volume C_v are defined as the amount of heat necessary to raise the temperature, in other words, the rate of change $C_p \equiv (\Delta Q/\Delta T)_p$ and $C_v \equiv (\Delta Q/\Delta T)_v$.

It is important to highlight that adiabatic processes are perfectly possible to be carried out in practice, one way to do it is by isolating the system with thermal insulating materials, but there is no perfect thermal insulation. The other way to do it is more plausible, we can make the process occur very fast for the system to not have enough time to exchange heat with the environment, this is what is done in car engines, for example.

Although some cycles are composed of irreversible processes, any thermal machine can be reversed and be turned into a refrigerator. This may look contradictory, but it is enough to consider an irreversible compression (expansion) instead of an irreversible expansion (compression) or maybe we could control the heat transfer from the cold reservoir instead of extracting heat from the hot reservoir, and so on. Despite we have irreversible processes, nothing prevents us to substitute each irreversible process with its opposite (also irreversible) process and construct a new machine that operates as a refrigerator.

1.1.2 Finite-Time Thermodynamics

There is another important quantity of the thermal machines that were left out. This quantity is the *power output P*, which is defined as the rate at which work W is performed over time

$$P = \frac{\Delta W}{\Delta t}. \tag{1.8}$$

Actually, for practical purposes, this quantity is even more important than the efficiency of the machine. The reason is clear, thinking about a car engine, we are more interested in driving at 100 km/h at a higher cost than driving at 1 km/h, no matter how much fuel we could save with this latter more efficient engine. If we think about the Carnot engine idealized in the previous section, this problem takes enormous proportions because we have quasistatic processes that take infinite time ($t \to \infty$) to occur, which means, by means of equation 1.8, that we have a zero power output at the end of the cycle ($P \to 0$).

As we have said in the previous section, the adiabatic process can be realizable in a finite time, so the problem rests in the isothermal processes of the Carnot cycle. How can we accelerate them? We must take into account the finite time at which heat is exchanged between the heat reservoirs and the working material.

We assume that the working substance is inside a vessel with diathermal walls. If we put the system (working substance + vessel) in contact with a reservoir, it will exchange heat according to Fourier's law of heat conduction. This law states that the rate of heat conduction is proportional to the temperature difference between the objects in contact

$$\dot{Q} = kA\frac{\Delta T}{\Delta x}, \tag{1.9}$$

where $\dot{Q}$ is the heat flux, k is the thermal conductivity of the material, A is the cross-sectional surface area of contact, ΔT the temperature difference, and Δx the thickness of the material.

We are interested in the isothermal processes in the Carnot cycle, so the heat flux $\dot{Q}_h$ during the isothermal expansion is given by

$$\dot{Q}_h = \alpha(T_h - T_{hw}), \tag{1.10}$$

where T_h is the temperature of the heat source and T_{hw} is the temperature of the working substance at this stage. Comparing with equation (1.9), the terms that depends on the properties of the material are all accounted in the coefficient α. Conversely, the isothermal compression gives us

$$\dot{Q}_c = \beta(T_c - T_{cw}), \tag{1.11}$$

where β is the heat transfer coefficient associated with the compression, T_c is the temperature of the heat sink and T_{cw} is the temperature of the working substance at this stage. If the isothermal expansion lasts a time t_h, the total heat absorbed during this stage by the working substance throughout the walls of the vessel is the integral of the heat flux $\dot{Q}_h$

$$Q_h = \dot{Q}_h t_h = \alpha t_h (T_h - T_{hw}), \tag{1.12}$$

where we have used equation (1.10) and the fact that the RHS of this equation has no dependence in time. On the other hand, for the isothermal compression, a similar calculation gives us the total heat Q_c released to the heat sink

$$Q_c = \dot{Q}_c t_c = \beta t_c (T_c - T_{cw}), \tag{1.13}$$

where t_c is the time it takes for the process to occur.

We may have accelerated the processes, but we still want our engine to be reversible, and this is the crucial argument for the statement of the *endoreversible engines* [29–32]. We need to leave the irreversible heat conduction out of play, to do so we establish a subsystem given by a central compartment, which is responsible for the work-delivering and heat-interacting operations. Outside of this central compartment, we have two heat exchangers connected to the heat reservoirs where the heat conduction occurs, these heat exchangers do the role of channels for delivering heat in and out of the subsystem. Therefore, the system as a whole operates irreversibly, but the internal compartment operates reversibly[5] (that is the reason why we call this engines "*endo-reversible*"). This condition ensures that equation (1.6) is

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[5]There is an interesting discussion about the validity of these arguments in Refs. [33–35]

still valid and if we compare it with equation (1.3), we have the following condition

$$\frac{Q_c}{Q_h} = -\frac{T_{cw}}{T_{hw}},$$

where we use the temperatures T_{cw} and T_{hw}, not the temperatures of the reservoirs T_h and T_c, because we are using the reversibility of the internal compartment[6]. Rearranging the terms,

$$\frac{Q_h}{T_{hw}} = -\frac{Q_c}{T_{cw}}. \tag{1.14}$$

This condition is fundamental and controversy, but we will let this discussions off the table for now. Therefore, we may substitute equations (1.12) and (1.13) in (1.14) to obtain

$$\frac{\alpha t_h(T_h - T_{hw})}{T_{hw}} = -\frac{\beta t_c(T_c - T_{cw})}{T_{cw}} = \frac{\beta t_c(T_{cw} - T_c)}{T_{cw}},$$

or

$$\frac{t_h}{t_c} = \frac{\beta T_{hw}(T_{cw} - T_c)}{\alpha T_{cw}(T_h - T_{hw})} \equiv \frac{\beta(T_h - x)y}{\alpha(T_c + y)x}, \tag{1.15}$$

where we define $x \equiv T_h - T_{hw}$ and $y \equiv T_{cw} - T_c$ to simplify the calculus. The total time spent in the isothermal processes is $t_h + t_c$ whereas for the adiabatics, say, we spent a total time $(\gamma - 1)(t_h + t_c)$ such that $\Delta t = \gamma(t_h + t_c)$ is the total time spent by the engine in the four processes to complete a single cycle with γ being an arbitrary coefficient. The total power output P is then

$$P = \frac{\Delta W}{\Delta t} = \frac{Q_h + Q_c}{\gamma(t_h + t_c)}, \tag{1.16}$$

where we have used equation (1.2) for the total work done by an engine. We can then use the expressions for Q_h and Q_c (equations 1.12 and 1.13) in the previous equation for the power output:

$$P = \frac{\alpha t_h(T_h - T_{hw}) + \beta t_c(T_c - T_{cw})}{\gamma(t_h + t_c)},$$

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[6]Lavenda's paper [36] criticize this condition, he states that the temperatures T_{hw} and T_{cw} of the system must be replaced by the temperatures of the heat reservoirs T_h and T_c.

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or, in terms of x and y,

$$P = \frac{\alpha t_h x - \beta t_c y}{\gamma(t_h + t_c)} = \frac{\alpha t_h x - \beta t_c y}{\gamma t_c(\frac{t_h}{t_c} + 1)} = \frac{\alpha x \frac{t_h}{t_c} - \beta y}{\gamma(\frac{t_h}{t_c} + 1)}.$$

Using the equation (1.15) to eliminate t_h/t_c, we obtain

$$\begin{aligned}
P &= \left[\alpha x \left(\frac{\beta(T_h - x)y}{\alpha(T_c + y)x}\right) - \beta y\right]\left[\gamma\left(\frac{\beta(T_h - x)y}{\alpha(T_c + y)x} + 1\right)\right]^{-1} \\
&= \beta y\left(\frac{T_h - x}{T_c + y} - 1\right)\left[\gamma\left(\frac{\beta(T_h - x)y}{\alpha(T_c + y)x} + 1\right)\right]^{-1} \\
&= \beta y\left(\frac{T_h - x}{T_c + y} - \frac{T_c + y}{T_c + y}\right)\left[\gamma\left(\frac{\beta y(T_h - x)}{\alpha x(T_c + y)} + \frac{\alpha x(T_c + y)}{\alpha x(T_c + y)}\right)\right]^{-1} \\
&= \beta y \frac{T_h - T_c - x - y}{T_c + y} \frac{\alpha x(T_c + y)}{\gamma[\beta T_h y + \alpha T_c x + xy(\alpha - \beta)]},
\end{aligned}$$

which leads us to

$$P = \frac{\alpha\beta xy(T_h - T_c - x - y)}{\gamma[\beta T_h y + \alpha T_c x + xy(\alpha - \beta)]}. \tag{1.17}$$

This is the power output of an endoreversible Carnot engine operating with finite time isothermal processes. But we are interested in obtaining the *maximum* power output for the Carnot engine, so we need to maximize the power function P for the temperatures T_h and T_c of the reservoirs. For this, we note that x and y will be the only variables of the system to be optimized. Thus, to maximize P, we need the conditions $\partial P/\partial x = 0$ and $\partial P/\partial y = 0$ to be satisfied, which leads us to

$$0 = \frac{\partial P}{\partial x} = \frac{\alpha\beta y(T_h - T_c - x - y) - \alpha\beta xy}{\gamma[\beta T_h y + \alpha T_c x + xy(\alpha - \beta)]} - \frac{\alpha\beta xy(T_h - T_c - x - y)[\alpha T_c + y(\alpha - \beta)]}{\gamma[\beta T_h y + \alpha T_c x + xy(\alpha - \beta)]^2},$$

so

$$[(T_h - T_c - x - y) - x](\beta T_h y + \alpha T_c x + xy(\alpha - \beta)) - x(T_h - T_c - x - y)[\alpha T_c + y(\alpha - \beta)] = 0,$$

simplifying some terms,

$$\beta T_h y(T_h - T_c - x - y) - x[\beta T_h y + \alpha T_c x + xy(\alpha - \beta)] = 0,$$

or

$$\beta T_h y(T_h - T_c - x - y) = x[\beta T_h y + \alpha T_c x + xy(\alpha - \beta)]. \tag{1.18}$$

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An analogous calculation for the condition $\partial P/\partial y = 0$ gives us

$$\alpha T_c x(T_h - T_c - x - y) = y[\beta T_h y + \alpha T_c x + xy(\alpha - \beta)]. \qquad (1.19)$$

Taking the ratio of equation (1.19) over equation (1.18) gives us

$$\frac{\alpha T_c x}{\beta T_h y} = \frac{y}{x},$$

or

$$y^2 = \frac{\alpha T_c x^2}{\beta T_h},$$

and, taking the positive square root, we get

$$y = \sqrt{\frac{\alpha T_c}{\beta T_h}} x. \qquad (1.20)$$

The minus square root would lead us to non-physical results (remember that $x = T_h - T_{hw} > 0$ and $y = T_{cw} - T_c > 0$, otherwise the heat would not flow from the source to the sink) and, for that reason, is not considered. Adding this result to equation (1.18), we get

$$\beta T_h \sqrt{\frac{\alpha T_c}{\beta T_h}} x \left(T_h - T_c - x - \sqrt{\frac{\alpha T_c}{\beta T_h}} x\right) = x\left[\beta T_h \sqrt{\frac{\alpha T_c}{\beta T_h}} x + \alpha T_c x + x\sqrt{\frac{\alpha T_c}{\beta T_h}} x(\alpha - \beta)\right],$$

or

$$\sqrt{\alpha \beta T_h T_c}\left(T_h - T_c - x - \sqrt{\frac{\alpha T_c}{\beta T_h}} x\right) = \sqrt{\alpha \beta T_h T_c} x + \alpha T_c x + x^2 \sqrt{\frac{\alpha T_c}{\beta T_h}}(\alpha - \beta).$$

Rewriting this equation in terms of $\mu \equiv x/T_h$,

$$T_h - T_c - \mu T_h\left(1 + \sqrt{\frac{\alpha T_c}{\beta T_h}}\right) = \mu T_h + \mu T_h \sqrt{\frac{\alpha T_c}{\beta T_h}} + \frac{\mu^2 T_h}{\beta}(\alpha - \beta).$$

Rearranging the terms, we obtain the quadratic equation

$$\left[1 - \frac{\alpha}{\beta}\right]\mu^2 - 2\left[\sqrt{\frac{\alpha T_c}{\beta T_h}} + 1\right]\mu + \left[1 - \frac{T_c}{T_h}\right] = 0, \qquad (1.21)$$

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whose solution is

$$\mu = \frac{2\left(\sqrt{\frac{\alpha T_c}{\beta T_h}}+1\right) \pm \sqrt{\left(4\frac{\alpha T_c}{\beta T_h}+1+2\sqrt{\frac{\alpha T_c}{\beta T_h}}\right)-4\left(1-\frac{\alpha}{\beta}\right)\left(1-\frac{T_c}{T_h}\right)}}{2\left(1-\frac{\alpha}{\beta}\right)}$$

$$= \frac{\frac{\sqrt{\alpha T_c}+\sqrt{\beta T_h}}{\sqrt{\beta T_h}} \pm \sqrt{2\sqrt{\frac{\alpha T_c}{\beta T_h}}+\left(\frac{T_c}{T_h}+\frac{\alpha}{\beta}\right)}}{\left(1-\sqrt{\frac{\alpha}{\beta}}\right)\left(1+\sqrt{\frac{\alpha}{\beta}}\right)}$$

$$= \frac{\frac{\sqrt{\alpha T_c}+\sqrt{\beta T_h}}{\sqrt{\beta T_h}} \pm \left(\sqrt{\frac{T_c}{T_h}}+\sqrt{\frac{\alpha}{\beta}}\right)}{\left(1-\sqrt{\frac{\alpha}{\beta}}\right)\left(1+\sqrt{\frac{\alpha}{\beta}}\right)}$$

$$= \frac{\sqrt{\alpha T_c}+\sqrt{\beta T_h} \pm \left(\sqrt{\beta T_c}+\sqrt{\alpha T_h}\right)}{\left(1-\sqrt{\frac{\alpha}{\beta}}\right)\left(1+\sqrt{\frac{\alpha}{\beta}}\right)\sqrt{\beta T_h}}$$

$$= \frac{\sqrt{T_h}(\sqrt{\beta} \pm \sqrt{\alpha})+\sqrt{T_c}(\sqrt{\alpha} \pm \sqrt{\beta})}{\left(1-\sqrt{\frac{\alpha}{\beta}}\right)\left(1+\sqrt{\frac{\alpha}{\beta}}\right)\sqrt{\beta T_h}}.$$

From this point on, we can separate the solution in two:

$$\mu_+ = \frac{\sqrt{T_h}(\sqrt{\beta}+\sqrt{\alpha})+\sqrt{T_c}(\sqrt{\alpha}+\sqrt{\beta})}{\left(1-\sqrt{\frac{\alpha}{\beta}}\right)\left(1+\sqrt{\frac{\alpha}{\beta}}\right)\sqrt{\beta T_h}} = \frac{1+\sqrt{\frac{T_c}{T_h}}}{1-\sqrt{\frac{\alpha}{\beta}}} > 1, \tag{1.22}$$

and

$$\mu_- = \frac{\sqrt{T_h}(\sqrt{\beta}-\sqrt{\alpha})+\sqrt{T_c}(\sqrt{\alpha}-\sqrt{\beta})}{\left(1-\sqrt{\frac{\alpha}{\beta}}\right)\left(1+\sqrt{\frac{\alpha}{\beta}}\right)\sqrt{\beta T_h}} = \frac{1-\sqrt{\frac{T_c}{T_h}}}{1+\sqrt{\frac{\alpha}{\beta}}} < 1. \tag{1.23}$$

The positive solution μ_+ is clearly non-physical because $\mu = x/T_h = 1 - T_{hw}/T_h < 1$, thus equation (1.23) must be the correct solution. Putting this result into equation (1.20), we get

$$y = \sqrt{\frac{\alpha T_c}{\beta T_h}}T_h\frac{1-\sqrt{\frac{T_c}{T_h}}}{1+\sqrt{\frac{\alpha}{\beta}}} = \frac{\sqrt{\frac{T_h}{T_c}}-1}{1+\sqrt{\frac{\beta}{\alpha}}}T_c. \tag{1.24}$$

Finally, the efficiency of the Carnot engine at maximum power output is given by

$$\eta = 1 - \frac{T_{cw}}{T_{hw}} = 1 - \frac{T_c+y}{T_h-x}. \tag{1.25}$$

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Using equations (1.23) and (1.24), we obtain

$$\eta = 1 - \frac{T_c + \frac{\sqrt{\frac{T_h}{T_c}}-1}{1+\sqrt{\frac{\beta}{\alpha}}}T_c}{T_h - T_h\frac{1-\sqrt{\frac{T_c}{T_h}}}{1+\sqrt{\frac{\alpha}{\beta}}}}$$

$$= 1 - \frac{T_c}{T_h}\frac{\left(\sqrt{\frac{\beta}{\alpha}}+\sqrt{\frac{T_h}{T_c}}\right)\left(1+\sqrt{\frac{\alpha}{\beta}}\right)}{\left(\sqrt{\frac{\alpha}{\beta}}+\sqrt{\frac{T_c}{T_h}}\right)\left(1+\sqrt{\frac{\beta}{\alpha}}\right)}$$

$$= 1 - \frac{T_c}{T_h}\frac{\sqrt{\beta T_h}}{\sqrt{\alpha T_c}}\sqrt{\frac{\alpha}{\beta}},$$

which leads us to

$$\eta_{CA} = 1 - \sqrt{\frac{T_c}{T_h}}. \tag{1.26}$$

This equation is known as the Curzon-Ahlborn (CA) efficiency and is the main result that we wanted to demonstrate. Despite this formula takes the names of F.L. Curzon and B. Ahlborn for a paper published in 1975 [29], they were not the first ones to obtain it. Novikov [37] and Yvon [38] obtained equation (1.26) some time before, assuming the temperature of the working substance was given by the geometric mean $T_m = \sqrt{T_c T_h}$, far away from the endoreversible model. But their result was not surprising, Thomson already showed many years before that the performance of an engine with an unequally heated system is optimized if the temperature of the system is exactly the geometric mean T_m [39].

Within the framework of *linear irreversible thermodynamics* (which was an important milestone in the development of nonequilibrium thermodynamics) and without the endoreversibility assumption, Van den Broeck showed in 2005 [40] that the efficiency of an engine at maximum power output is bounded from above by the CA efficiency. Yet in the context of irreversible thermodynamics, three years after the paper of Broeck was published, in 2008, Schmiedl and Seifert (SS) derived a different expression for the efficiency at maximum power output [41]:

$$\eta_{SS} = \frac{\eta_C}{2 - \alpha\eta_C}, \tag{1.27}$$

with α being associated with dissipative coupling to the hot and cold reservoirs. Only in

2012, this discrepancy of results was solved, Y. Apertet and coworkers published a paper [42] clarifying that η_{CA} and η_{SS} has different configurations: η_{CA} is associated with *endoreversibility*, where dissipations are present in the connections to the thermal reservoirs, and η_{SS} is associated with *exoreversibility*, where dissipations are present in the energy conversion itself. Five years later, in 2017, also with Y. Apertet and coworkers, it was found a more general expression for the efficiency at maximum power, beyond the scope of linear heat engines, that recover the efficiencies η_{CA} and η_{SS} as special cases of this more general one, particularly, the CA efficiency is showed to be associated with a particular case of nonlinear heat engines [43].

To put and end to this section, coming back to the result (1.26) and leaving these discussions aside, we can obtain the maximum power P_{max} by substituting equations (1.23) and (1.24) into (1.17). After some algebraic juggling we obtain

$$P_{max} = \frac{\alpha\beta}{\gamma}\left(\frac{\sqrt{T_h} - \sqrt{T_c}}{\sqrt{\alpha} + \sqrt{\beta}}\right)^2.\tag{1.28}$$

1.1.3 Clausius Theorem and The Third Law of Thermodynamics

During fifteen years, Rudolf Clausius wrote nine memoirs about the motive power of heat, which was later collected and published as a book entitled *Mechanical Theory of Heat* [44]. In his sixth memoir, first published in 1862, Clausius settled the foundations of an important theorem that establish a mathematical expression for understanding the second law of thermodynamics. He states that "[...] the algebraic sum of all the transformations occurring in a cyclical process can only be less than zero, or, as an extreme case, equal to nothing", in mathematical terms, we have the following expression valid for any cyclic process

$$\oint \frac{\mathrm{d}Q}{T} \leq 0,\tag{1.29}$$

where the equality holds for any reversible process, dQ is the energy flow into the system and T is the temperature of the system when that energy is absorbed. As an corollary for

this theorem, for any reversible process (not necessarily cyclic) operating from state A to state B, the quantity

$$\int_A^B \frac{dQ}{T}$$

is conservative, i.e., is the same for any path segment γ that starts at A and ends at B. Indeed, if we take two reversible paths γ_1 and γ_2 that connects A and B, and we start a cycle from A following the path γ_1 until we get to B and then go back to A following the path γ_2, we will have, using equation (1.29), the following

$$\int_{A \atop \gamma_1}^B \frac{dQ}{T} + \int_{B \atop \gamma_2}^A \frac{dQ}{T} = 0,$$

but,

$$\int_{B \atop \gamma_2}^A \frac{dQ}{T} = -\int_{A \atop \gamma_2}^B \frac{dQ}{T},$$

so,

$$\int_{A \atop \gamma_1}^B \frac{dQ}{T} = \int_{A \atop \gamma_2}^B \frac{dQ}{T}.$$

Thus, it is a conservative quantity and does not depend on the reversible path we choose. This quantity can be defined as a state function S that depends only on the initial and final states A and B

$$\int_A^B \frac{dQ}{T} = S(B) - S(A), \tag{1.30}$$

with

$$S(X) = \int_0^X \frac{dQ}{T} \tag{1.31}$$

being the *entropy*[7] of an arbitrary state X and 0 is a state of reference. An alternative formulation of the second law of thermodynamics is that the entropy of an isolated system never decreases

$$\Delta S \geq 0. \tag{1.32}$$

This follows from equations (1.29) and (1.30), because in an isolated system, $dQ = 0$, so

$$\Delta S = S(B) - S(A) \geq \int_A^B \frac{dQ}{T} = 0.$$

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[7]A name coined by Clausius in 1865, which comes from the greek "*transformation*".

The state of reference mentioned before in equation (1.31) is very complex to be defined because we need it to be accessible for any system simultaneously. Only with the work of the German chemist Walther Nernst at the beginning of the 20th century it was possible to overcome this problem. Nernst theorem states that the entropy for any system in *thermodynamic equilibrium* goes to zero as the absolute temperature of this system approaches the absolute zero:

$$\lim_{T \to 0} \Delta S = 0. \tag{1.33}$$

This is a modern formulation of the Nernst theorem that was later used by Max Planck and nowadays is known as the third law of thermodynamics, although Nernst's first formulations avoided completely the concept of entropy. Therefore, this state of zero absolute temperature is the perfect state of reference that we were looking for because the entropy is the same for any system at this point.

1.1.4 Entropy and Helmholtz free energy

We have said that entropy is a state function, but we also need it to be an extensive quantity, i.e., entropy must increase as we enlarge the system, if we mix two gases in equilibrium, for example, the entropy of the resulting mixed gas must be the sum of the entropy of each individualized gas before we mix the gases[8]. Hereupon, the entropy must depend only on extensive thermodynamic quantities like energy (U), volume (V), and the number of particles (N), that is, $S = S(U, V, N)$. Differentiating it, we obtain

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN \tag{1.34}$$

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[8]Actually, this specific situation lead Gibbs to formulate a famous paradox, he calculated the entropy of the mixed gas and the resulting entropy was less than the sum of the entropy of the individual gases before the mixing, thus violating the second law of thermodynamics. This paradox was "*solved*" introducing ad hoc a correction factor $N!$ that was only explained years later with the arising of quantum mechanics.

On the other hand, the internal energy must be a function $U = U(S, V, N)$ and, from the first law of thermodynamics

$$dU = TdS - pdV + \mu dN, \tag{1.35}$$

or, isolating dS,

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN, \tag{1.36}$$

where $\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$ is called the *chemical potential*, $TdS = dQ$ is the infinitesimal heat exchanged (with T being the absolute temperature) and $pdV = dW$ the infinitesimal work done (with p being the pressure). Comparing equations (1.34) and (1.36), we get the equations of state

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}, \tag{1.37}$$

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N}, \tag{1.38}$$

$$\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{U,V}. \tag{1.39}$$

An also important quantity for thermodynamics is the Helmholtz free energy F, which is defined as

$$F = U - TS, \tag{1.40}$$

and is a function $F = F(T, V, N)$. In simple words, the free energy is the *useful* energy available to be extracted out of the system as work. Note that, as we increase the entropy S the free energy F decreases, so the entropy does act as an exhauster of *useful* energy, although no energy is lost. We also have another alternative formulation of the second law of thermodynamics in contrast with equation (1.32), for an isolated system at constant temperature and volume the free energy never increases

$$\Delta F \leq 0. \tag{1.41}$$

1.1.5 Thermodynamic potentials

We may generally classify the most common thermodynamic potentials in five: the internal energy U, the Helmholtz free energy F, the enthalpy H, the Gibbs free energy G and the grand potential Φ_G.

The internal energy has the following natural variables (S, V, N) and is given by

$$U = TS - pV + \mu N, \tag{1.42}$$

or, in the standard differential form (equation 1.35),

$$dU = TdS - pdV + \mu dN. \tag{1.43}$$

The Helmholtz free energy has the following natural variables (T, V, N) and is given by (equation 1.40)

$$F = U - TS, \tag{1.44}$$

or, in the standard differential form,

$$dF = -SdT - pdV + \mu dN. \tag{1.45}$$

The enthalpy has the following natural variables (S, p, N) and is given by

$$H = U + pV, \tag{1.46}$$

or, in the standard differential form,

$$dH = TdS + Vdp + \mu dN. \tag{1.47}$$

The Gibbs free energy has the following natural variables (T, p, N) and is given by

$$G = U + pV - TS, \tag{1.48}$$

or, in the standard differential form,

$$dH = -SdT + Vdp + \mu dN. \tag{1.49}$$

The grand potential has the following natural variables (T, V, μ) and is given by

$$\Phi_G = U - TS - \mu N, \tag{1.50}$$

or, in the standard differential form,

$$d\Phi_G = -SdT - pdV - Nd\mu. \tag{1.51}$$

There are three equations of state for each thermodynamic potential and they can be obtained in the same way as we did for the entropy in subsection 1.1.4.

1.2 Statistical Mechanics

Thermodynamics is a phenomenological theory based upon empirical facts that justify its laws. On the other hand, statistical mechanics tries to explain the macroscopic aspects of thermodynamics starting from a microscopic description of the atomic or molecular structure of matter in equilibrium in the same empirical sense used in thermodynamics [45, 46]. Here, equilibrium is to be understood as *statistic equilibrium* and it does not mean that the particles have stopped moving, rather, only that the ensemble of particles as a whole is not evolving in time.

We may broadly classify any equilibrium system in statistical mechanics in three different ensembles: the microcanonical, canonical, and grand canonical ensembles.

1.2.1 Microcanonical ensemble

The microcanonical ensemble is characterized by an isolated system with a huge number N of particles occupying a large volume V. By requiring the system to be isolated, we mean that the energy is a constant of motion. Since we have N particles moving in three directions, we may introduce a $6N$-dimension phase space, or Γ space, of the system with $3N$ canonical coordinates $q_1, q_2, ..., q_{3N}$ and $3N$ canonical momenta $p_1, p_2, ..., p_{3N}$. The points in phase

space represent microscopic states of the system, i.e., each point is a possible configuration for the particles to be distributed. Depending on these microscopic configurations, the system assumes different macroscopic states. Note that for any macroscopic state, we may have an infinite number of microscopic states that satisfy the macroscopic constraints (e.g. the energy or the volume of the system remains the same by a permutation of the positions of two particles).

Classical statistical mechanics is sustained in the *equal a priori probability postulate*. This postulate states that when a macroscopic system is in thermodynamic equilibrium, then all of the microscopic states that satisfy the macroscopic conditions have the same probability for the system to be found in. To justify this postulate, we recall here Laplace's "Principle of Insufficient Reason", in which one said that two events are to be assigned equal probabilities if there is no reason to think otherwise [47].

The number of microscopic states of an ensemble with energy E, volume V and number of particles N, subjected to $\{X_i\}$ constraints is given by the function $W(E, V, N; \{X_i\})$. Since every microscopic state that satisfies the macroscopic conditions is equally probable to be found, then the probability $P\{X_i\}$ of finding the system with the constrains $\{X_i\}$ must be directly proportional to the number of microscopic states with these constraints, i.e.,

$$P\{X_i\} \propto W(E, V, N; \{X_i\}).$$

In order to correctly interpret the above expression as a probability, we must normalize it

$$P\{X_i\} = \frac{W(E, V, N; \{X_i\})}{\sum_{\{X_i\}} W(E, V, N; \{X_i\})}, \tag{1.52}$$

where the sum in the denominator is a sum over all possible constraints $\{X_i\}$. This way the probability of finding the system with any possible constraint that satisfies the global constraints (E, V, N) is the sum $\sum_{\{X_i\}} P\{X_i\} = 1$.

Let us separate our system in two different subsystems by an adiabatic, fixed and impermeable wall. The total number of accessible microscopic states for the composite system is

the product

$$W(E = E_1 + E_2) = W_1(E_1)W_2(E_2), \qquad (1.53)$$

where $W_1(E_1)$ and $W_2(E_2)$ are the number of accessible microscopic states in the subsystem (1) and (2), respectively. If we now let the separating wall to be diathermic, the energies E_1 and E_2 can fluctuate as long as $E = E_1 + E_2$, where E is the total energy of the composite system. From equations (1.52) and (1.53), the probability of finding the composite system in a state where the subsystem (1) has energy E_1 is[9]

$$P(E_1) = \frac{W(E_1; E)}{\sum_{E_1=0}^{E} W(E_1; E)} = \frac{W_1(E_1)W_2(E - E_1)}{\sum_{E_1=0}^{E} W_1(E_1)W_2(E - E_1)}. \qquad (1.54)$$

In general, increasing the energy E will lead to an increase in the number of states $W(E)$. This way $W_1(E_1)$ increases while $W_2(E - E_1)$ decreases, which implies that the probability $P(E_1)$ must assume a maximum value. For convenience, let us take the logarithmic of $P(E_1)$ and use the condition for a maximum

$$0 = \frac{\partial \ln P(E_1)}{\partial E_1} = \frac{\partial \ln W_1(E_1)}{\partial E_1} + \frac{\partial \ln W_2(E - E_1)}{\partial E_1} = \frac{\partial \ln W_1(E_1)}{\partial E_1} - \frac{\partial \ln W_2(E_2)}{\partial E_2}, \qquad (1.55)$$

where we used the fact that the denominator of equation (1.54) is a constant (has zero derivative) and also that $E_1 = E - E_2$. This equation is the condition for finding the most probable energy E_1 of the subsystem (1) given the total energy $E = E_1 + E_2$. Equation (1.55) is also revealing us an important condition in thermodynamics, but to comprehend it, we need to establish the statistical connection with thermodynamics.

Boltzmann introduced the entropy as a function of the number of accessible microscopic states

$$S(E) = k_B \ln W(E), \qquad (1.56)$$

where k_B is the Boltzmann constant. If the system has a determined microscopic state $(W(E) = 1)$, the entropy for this system is null, which sustains the interpretation of entropy

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[9]The sum $\sum_{E_1=0}^{E}$ requires the energies to be discretized, but it is also possible to generalize to it to the continuous case [48].

as a measure of uncertainty. Note that equation (1.53) shows that the system increases its number of states in a multiplicative way, but entropy will follow this growth linearly, obeying the extensive property, i.e.,

$$S(E = E_1 + E_2) = k_B \ln W(E_1) + k_B \ln W(E_2) = S(E_1) + S(E_2). \tag{1.57}$$

Recalling equation (1.37), the temperature of the system can now be introduced. We then recognize the derivatives in equation (1.55) exactly, except for a multiplicative constant, as the temperatures of the subsystems, that is, $T_1 = \partial S(E_1)/\partial E_1$ and $T_2 = \partial S(E_2)/\partial E_2$. This indicates that the condition for the maximum probability is also the condition for thermodynamic equilibrium in the sense that the subsystems has the same temperature $T_1 = T_2$.

1.2.2 Canonical and Grand canonical ensembles

Putting aside the idealization of a complete isolated system as it was required in the microcanonical ensemble, we may let our system thermalize with a larger system, the heat reservoir. The canonical ensemble is characterized by a system isolated by diathermic walls that allow energy fluctuations, but no particle exchange with the reservoir is allowed. The *partition function* is defined as the volume of the 6N-dimensional phase space occupied by the canonical ensemble:

$$Z_N(V,T) = \frac{1}{N! h^{3N}} \int \mathrm{d}^{3N}p \int \mathrm{d}^{3N}q \exp[-\beta \mathcal{H}(p,q)], \tag{1.58}$$

where the factor $N! h^{3N}$ is introduced ad-hoc at first and can only be explained in the context of quantum mechanics with the emergence of quantum statistical mechanics. The number of particles N, the volume V, and the temperature T of the ensemble remain fixed as the energy fluctuates. The factor β is sometimes called the inverse temperature and is defined as $\beta = 1/k_B T$, and $\mathcal{H}(p,q)$ is the Hamiltonian of the system. If the energy is discretized,

the partition function is given by the sum

$$Z = \sum_k e^{-E_k/k_B T}, \tag{1.59}$$

where E_k are the discretized energies. Following the logic behind equation (1.54), the probability of finding our system with energy E_j is given by

$$P_j = \frac{\exp(-\beta E_j)}{\sum_k \exp(-\beta E_k)}. \tag{1.60}$$

The connection with thermodynamics is given by the Helmholtz free energy (see equation 1.44)

$$F = -k_B T \ln Z_N(V, T). \tag{1.61}$$

Substituting equation (1.59) into the Helmholtz free energy, we obtain

$$F = -k_B T \ln \sum_k e^{-E_k/k_B T}. \tag{1.62}$$

From equation (1.45), we have the following expression for the entropy

$$S = -\frac{\partial F}{\partial T} = k_B \ln Z_N + \frac{1}{T Z_N} \sum_k E_k e^{-E_k/k_B T}. \tag{1.63}$$

Equation (1.60) enables us to write

$$-\beta E_j = \ln(Z_N P_j). \tag{1.64}$$

Putting this into equation (1.63), we get

$$S = k_b \ln(Z_N P_j) \frac{\sum_k E_k e^{-E_k/k_B T}}{Z_N} - k_B \sum_k \frac{e^{-\beta E_k}}{Z_N}(-\beta E_k)$$

$$= -k_B \sum_k \frac{e^{-\beta E_k}}{Z_N} \ln \left[\frac{\exp(-\beta E_j)}{Z_N} \right],$$

or simply,

$$S = -k_B \sum_k P_k \ln P_k. \tag{1.65}$$

This expression is known as the Gibbs entropy, but in light of information theory, it is also known as the Shannon entropy [49]. Exactly as the Boltzmann entropy, equation (1.56), it

measures the microstates available to a system, but it has an advantage in contrast to the Boltzmann entropy, it does not require the system to be in a single well-defined macrostate. This way, the Gibbs entropy is seen as a generalization of the Boltzmann entropy holding for all systems, while the Boltzmann entropy is only the entropy if the system is in global thermodynamical equilibrium.

The Grand canonical ensemble is the final generalization in classical statistical mechanics, it is characterized by a system delimited in a volume V in thermodynamic equilibrium with a reservoir of heat and particle. In other words, the ensemble is in thermal and chemical equilibrium with the reservoir. Thus, the temperature T and the chemical potential μ of the system are fixed, but the number of particles N and the energy E of the system can fluctuate. The *grand partition function* is the generalization of the partition function in canonical ensemble with the addition of accounting for all the possible configurations of particles in the system

$$\Xi(z, \beta) = \sum_{N=0}^{\infty} z^N Z_N(V, T), \tag{1.66}$$

with $z = \exp(\beta\mu)$ being the fugacity of the system. If the energy is discretized, the grand partition function is given by the sum

$$\Xi = \sum_k \exp(-\beta E_k + \beta\mu N_k) \tag{1.67}$$

where N_k are the number of particles of the system when the energy is E_k. The probability of finding our system with energy E_j and number of particles N_j is given by

$$P_j = \frac{1}{\Xi} \exp(-\beta E_j + \beta\mu N_j). \tag{1.68}$$

The connection with thermodynamics is given by the grand potential (see equation 1.50)

$$\Phi_G = -k_B T \ln \Xi(z, \beta). \tag{1.69}$$

1.3 Quantum statistical mechanics

Till now we have studied only the classical statistical mechanics, where almost all of its developments were a consequence of the classical laws of motion. Recalling the classical kinetic theory of gases, the classical statistical mechanics can be almost rigorously derived from molecular dynamics, except for the Boltzmann assumption of molecular chaos [45]. Nonetheless, all systems in nature obey quantum mechanics. Thus, there must be a more general theory valid in the quantum mechanics regime, where the classical statistical mechanics can be obtained in the corresponding limits. This theory is the *quantum statistical mechanics.*

The state of a quantum system, which is also the quantum microstate, is a vector $|\psi\rangle$ in infinite dimensional Hilbert space. An observable in quantum mechanics is a hermitian operator, which has real eigenvalues. Any state $|\psi\rangle$ can be written as a linear superposition of eigenstates of any observable. In particular, it can be expressed in terms of the energy eigenstates $|\psi_n\rangle$ of the Hamiltonian $\hat{H}$ of the system

$$|\psi\rangle = \sum_n c_n |\psi_n\rangle, \qquad (1.70)$$

where the coefficients c_n are in general time-dependent and the energy eigenstates $|\psi_n\rangle$ satisfies $\hat{H}|\psi_n\rangle = E_n |\psi_n\rangle$, with E_n being the eigenenergies. The expectation value of an observable $\hat{\mathcal{O}}$ is given by

$$\langle\hat{\mathcal{O}}\rangle = \frac{\langle\psi|\hat{\mathcal{O}}|\psi\rangle}{\langle\psi|\psi\rangle}. \qquad (1.71)$$

Using equation (1.70), the expectation value of $\hat{\mathcal{O}}$ can be written as

$$\langle\hat{\mathcal{O}}\rangle = \frac{\sum_m \sum_n c_m^* c_n \langle\psi_m|\hat{\mathcal{O}}|\psi_n\rangle}{\sum_m \sum_n c_m^* c_n \langle\psi_m|\psi_n\rangle} = \frac{\sum_m \sum_n c_m^* c_n \langle\psi_m|\hat{\mathcal{O}}|\psi_n\rangle}{\sum_n c_n^* c_n}, \qquad (1.72)$$

where we have used the orthonormality of $|\psi_n\rangle$. It is known that macroscopic systems are never perfectly isolated systems since they are always interacting with the environment, although in general this interaction is extremely weak. Therefore, since we are dealing with

an ensemble of particles, which are large (macroscopic) systems[10], the most rigorous thing to do is to consider in our calculations the state of the system plus the environment combined. The state (1.70) should be written as the following

$$|\psi\rangle = \sum_n b_n |\xi_n\rangle \otimes |\psi_n\rangle, \tag{1.73}$$

where the states $|\xi_n\rangle$ are representing the states of the environment. Despite equation (1.73) is the most correct way of considering the state of our system, equation (1.70) can still be a valid representation of the state $|\psi\rangle$ if we identify the coefficients c_n as $b_n |\xi_n\rangle$. Following this reasoning, equation (1.72) is also still valid, provided that the product $c_m^* c_n$ is identified as $b_m^* b_n \langle\xi_m|\xi_n\rangle$.

Equation (1.72) gives us the expectation value of the observable $\hat{\mathcal{O}}$ at any instant of time. However, we are interested here in measuring thermodynamic properties of an ensemble of particles and these measurements are never instantaneous. This way, what we are truly measuring is an average time value of the observable. Therefore, the correct quantity that we are actually measuring must be

$$\langle\hat{\mathcal{O}}\rangle = \frac{\overline{\langle\psi|\hat{\mathcal{O}}|\psi\rangle}}{\overline{\langle\psi|\psi\rangle}} = \frac{\sum_m \sum_n \overline{c_m^* c_n} \langle\psi_m|\hat{\mathcal{O}}|\psi_n\rangle}{\sum_n \overline{c_n^* c_n}}. \tag{1.74}$$

In general, the terms $\overline{c_m^* c_n}$ cannot be directly calculated, since they involve all the states of the environment, and its interaction with the system (remember that $c_n = b_n |\xi_n\rangle$), which makes the calculation extremely difficult. Faced with these difficulties in calculating these terms, we are now able to enunciate the postulates of quantum statistical mechanics. These postulates are concerned with the form of the coefficients $\overline{c_m^* c_n}$ when equation (1.74) refers to a macroscopic observable of a macroscopic system in thermodynamic equilibrium.

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[10]If you get confused here from the use of quantum mechanics in macroscopic systems, remember that the particles considered here are inherently quantum and quantum effects can be important even in the macroscopic regime. As an example, if we have a gas of free electrons, which are fermions, then things like Pauli's exclusion principle are important for them.

Previously we said that the system interacts weakly with the environment, this makes the energy of our system to be approximately constant. In other words, its energy must lie between E and $E + \Delta$ (with $\Delta \ll E$). This way we write the postulates of quantum statistical mechanics as the following

Postulate of Equal a Priori Probability

$$\overline{c_n^* c_n} = \begin{cases} 1 & (E < E_n < E + \Delta) \\ 0 & (\text{otherwise}) \end{cases} \tag{1.75}$$

Postulate of Random Phases

$$\overline{c_m^* c_n} = 0 \quad (m \neq n) \tag{1.76}$$

The postulate of equal a priori probability (equation 1.75) is telling us that the probability of finding any state $|\psi_n\rangle$ satisfying the constraint for energy is the same (equiprobable states) and that any state that does not satisfy the global constraint is not allowed to be found.

Unlike the postulate of equal a priori probability, the postulate of random phases brings a purely quantum contribution to the foundations of statistical mechanics. It is not enough that the energy eigenstates are equiprobable, these states must also be in an incoherent superposition, and equation (1.76) is telling us exactly this. The incoherent superposition is necessary because the system is weakly interacting with the environment without exchanging energy, this way the decoherence plays an important role in killing the quantum superpositions of energy eigenstates of the system.

As a consequence of these postulates the state $|\psi\rangle$ of the system be written as

$$|\psi\rangle = \sum_n a_n |\psi_n\rangle, \tag{1.77}$$

where

$$|a_n|^2 = \begin{cases} 1 & (E < E_n < E + \Delta) \\ 0 & (\text{otherwise}) \end{cases} \tag{1.78}$$

The expectation value for an observable $\hat{\mathcal{O}}$ may also be reformulated in terms of these coefficients a_n as the following

$$\langle \hat{\mathcal{O}} \rangle = \frac{\sum_m \sum_n |a_n|^2 \langle \psi_m | \hat{\mathcal{O}} | \psi_n \rangle}{\sum_n |a_n|^2}. \tag{1.79}$$

The ensemble defined by the previous postulates is the microcanonical ensemble.

At this point, it is interesting to reformulate the preceding discussion in term of the density operator, instead of quantum states. The density operator associated with the state $|\psi\rangle$ is defined by

$$\hat{\rho} = \frac{|\psi\rangle \langle \psi|}{\text{Tr}\{|\psi\rangle \langle \psi|\}}, \tag{1.80}$$

where $\text{Tr}\{...\}$ stands for the trace over a complete set of states. If $|\psi\rangle$ is normalized, then $\text{Tr}\{|\psi\rangle \langle \psi|\} = 1$. Using equation (1.77) together with (1.75) and (1.76), the density operator can be written as

$$\hat{\rho} = \sum_{E < E_n < E + \Delta} |\psi_n\rangle \langle \psi_n|. \tag{1.81}$$

Taking the trace of $\hat{\rho}$, we obtain the states whose energy lies between E and $E + \Delta$:

$$\text{Tr}\hat{\rho} \equiv \Gamma(E). \tag{1.82}$$

This way, the connection with thermodynamics is established with the identification of entropy as

$$S(E, V) = k_B \log \Gamma(E), \tag{1.83}$$

where V is the volume of the system and k_B is the Boltzmann's constant. In this formalism, the expectation value of an observable $\hat{\mathcal{O}}$ is given by

$$\langle \hat{\mathcal{O}} \rangle = \text{Tr}\{\hat{\rho}\hat{\mathcal{O}}\}. \tag{1.84}$$

Choosing the energy eigenstates of the system to take the trace, one gets

$$\langle \hat{\mathcal{O}} \rangle = \sum_n \langle \psi_n | \hat{\rho}\hat{\mathcal{O}} | \psi_n \rangle = \sum_n \langle \psi_n | \hat{\rho} \left(\sum_m |\psi_m\rangle \langle \psi_m| \right) \hat{\mathcal{O}} | \psi_n \rangle = \sum_{n,m} \rho_{nm} \langle \psi_m | \hat{\mathcal{O}} | \psi_n \rangle, \tag{1.85}$$

where we have used the completeness relation $\sum_m |\psi_m\rangle \langle\psi_m| = \hat{\mathbb{I}}$. The term $\rho_{nm} = \langle\psi_n| \hat{\rho} |\psi_m\rangle$ is called the density matrix of the system. Comparing equations (1.85) and (1.79), we recognize the density matrix as

$$\rho_{nm} = \frac{|a_n|^2}{\sum_n |a_n|^2}\delta_{nm}. \tag{1.86}$$

Using equation (1.78), we can also write the microcanonical density matrix as

$$\rho_{nm} = \begin{cases} \dfrac{1}{\Gamma(E)} & (E < E_n < E + \Delta) \\ \\ 0 & \text{(otherwise)} \end{cases} \tag{1.87}$$

The Canonical ensemble can be described following the same reasoning as in the classical statistical mechanics. The canonical density matrix is then

$$\rho_{nn} = \frac{e^{-\beta E_n}}{Z}, \tag{1.88}$$

where

$$Z = \sum_n e^{-\beta E_n} \tag{1.89}$$

is the canonical partition function and $\beta = 1/k_B T$. The elements out of the diagonal of the density matrix is zero. The ensemble average of the observable $\hat{\mathcal{O}}$ is then

$$\langle\hat{\mathcal{O}}\rangle = \frac{1}{Z}\sum_n e^{-\beta E_n} \langle\psi_n| \hat{\mathcal{O}} |\psi_n\rangle. \tag{1.90}$$

In contrast, the grand canonical ensemble is described by the density matrix

$$\rho_{ii} = \frac{e^{-\beta(E_i - \mu N_i)}}{\Xi}, \tag{1.91}$$

where

$$\Xi = \sum_i e^{-\beta(E_i - \mu N_i)} \tag{1.92}$$

is the grand canonical partition function and μ is the chemical potential. In short, the only assumptions we made were the two postulates of quantum statistical mechanics, and from them, we can even obtain all the laws of thermodynamics. This way, these postulates can be seen as something even more fundamental than the laws of thermodynamics.

1.4 Fundamental postulate of statistical mechanics

Even nowadays the foundations of statistical mechanics are still a subject of debate. At this point, we give a brief overview of the most controversial issue in statistical mechanics, which is the validity of the fundamental postulate of statistical mechanics: the postulate of equal a priori probability. Present in both classical and quantum perspectives, the only justification till now that we gave for this postulate was the principle of insufficient reason. However this assumption may appear just as arbitrary as any other that might be made, we have no reason to assign weights for the probabilities of certain microstates, but we also have no reason to consider all of them with the same probability weight.

With the great advance provided by the development of the information theory by Shannon, it is shown that the usual computational rules for the statistical mechanics, starting with the determination of the partition function, are an immediate consequence of the so-called *maximum-entropy principle* [47]. The work of Shannon gives the entropy a more general status, independent of thermodynamics. This enables us to take the entropy as our starting concept, in contrast to the previous approach where the identification with entropy was made only at the end to establish the connection with thermodynamics.

The principle of maximum entropy may be regarded as an extension of the principle of insufficient reason, and it states that the probability distribution $(p_1, ..., p_n)$ that better represents a system in equilibrium is the one in which the Shannon entropy $H(p_1, ..., p_n) = -\sum_i p_i \ln p_i$ is maximum. The advantage of the principle of maximum entropy is that it is a positive statement that accounts for every situation that is not absolutely excluded by the given information and determines uniquely the correct probability distribution, in contrast to the principle of insufficient reason that is based on the negative statement that "there was no reason to think otherwise".

Therefore, we are eliminating the only assumption of classical statistical mechanics not contained in the laws of mechanics. With this statement, the statistical mechanics is no

longer dependent on physical hypotheses and it seems now that it may be considered as a form of statistical inference rather than a physical theory.

Beyond the maximum-entropy principle, we also have the notion of typicality. In fact, there is a quantum-mechanical approach for the statistical mechanics where the postulate of equal a priori probability can be proved, not postulated [50]. This is done by simply considering the effect of entanglement between the system and its environment, which implies the lack of information that will give the canonical density matrix for the system. Thus the principle of equal a priori probability should be replaced by the principle of canonical typicality, where thermalization emerges as a consequence of typicality [51].

Chapter Two

Quantum Thermodynamics

In this chapter, we enter the main topic of this dissertation: the *quantum thermody-namics* and, in particular, the study of *quantum thermal machines*. We start our study by enunciating and discussing the many faces of the laws of quantum thermodynamics in several situations, which are a generalization toward the miniaturization into the quantum realm of operation. We then define what is now acceptable as a quantum heat engine for closed unitary dynamics and also for regimes beyond the equilibrium conditions, for that we state the quantum thermodynamical processes that compose the cycle of operation of the engines and we show what is the quantum analog of a Carnot and Otto cycle. We analyze the dynamics of the thermodynamics processes and how the friction appears as we acceler-ate these processes. We finish with a discussion about the violation of the thermodynamic Carnot bound for the efficiency of a heat engine.

2.1   The Laws of Quantum Thermodynamics

During the early development of solid state lasers, more precisely in 1959, Scovil and Schulz-DuBois published a paper in the famous Physical Review Letters where they identify that three-level masers can be regarded as heat engines [2]. The main conceptual difference between these and conventional heat engines is that the three-level maser presents a discrete

energy spectrum while the conventional heat engines operate with a continuous spectrum of energies. However, if a three-level maser can be regarded as a heat engine, which is a cyclical operation, then it can be reversed to operate as a refrigerator. Following this logic the Maser cooling was proposed still in 1959 [52] and, years later, in 1967, so was the Laser cooling [53]. Only in 1975 the work of Wineland and Hänsch [53, 54] reinvented Laser cooling in a way that does not mention any thermodynamic arguments.

This pioneering work by Scovil and Schulz-Dubois started the search for the quantum thermal machines, which was the beginning of the emergence of the whole research area of *quantum thermodynamics* [3, 5, 55].

We may ask ourselves, if the quantum statistical mechanics (QSM) is already a successful theory that, from only two fundamental postulates, recovers the laws of thermodynamics and also lead to definite formulas for all the thermodynamic functions of a given substance, why we would be concerned in searching for a *quantum thermodynamics* (QT) theory? Well, the theory of quantum thermodynamics is not interested in recovering the laws of thermodynamics in the macroscopic world from the microscopic world of quantum mechanics in the same way as the QSM does, the QT is mostly interested in obtaining a description of the laws of thermodynamics in the microscopic regime, the QT is interested in talking about heat, work, and entropy or even building a heat engine (a quantum one). Not only that, but the QT uses an important ingredient to study thermodynamical processes, which is the dynamics (a missing concept in the theory of QSM), here we are leaving with slow steps the close-to-equilibrium condition and we are entering into the theory of finite-time thermodynamics [56, 57] in the quantum mechanics framework.

2.1.1 The 0-Law

The zeroth law of thermodynamics is basically a transitivity relation pairwise between three objects: *If A and B are in thermal equilibrium with C, then A is also in thermal*

equilibrium with B. A thermal equilibrium condition is trivial in classical thermodynamics, if we put two macroscopic systems in contact they will exchange heat (from the hotter to the colder one), after waiting enough time they will thermalize (i.e., the energy flow will be interrupted) and reach the same temperature, so 'thermal equilibrium' condition is a synonym of 'equal temperature' condition.

When we go to the domain of quantum mechanics, things are not quite the same. First of all, we must separate two possible cases: When the quantum system is weakly coupled to a thermal bath such that there is no system-bath entanglement and the system can be fully described by local operators, and when the system is strongly coupled to a thermal bath, where there is a nonequilibrium evolution with no universal definition of temperature and we must appeal to trying to define effective temperatures at all times (which is not always a possibility).

System-bath weak coupling

If a quantum system is weakly coupled to a thermal bath obeying a Markovian dynamics, then the system and environment can be considered as uncorrelated during the evolution process and the system's density operator $\hat{\rho}_s$ evolution follows from Lindblad-Gorini-Kossakowski-Sudarshan (LGKS) master equation

$$\frac{d}{dt}\hat{\rho}_s(t) = -\frac{i}{\hbar}[\hat{H}_s, \hat{\rho}_s] + \sum_k \gamma_k \left(\hat{L}_k \hat{\rho}_s \hat{L}_k^\dagger - \frac{1}{2}\{\hat{L}_k^\dagger \hat{L}_k, \hat{\rho}_s\} \right), \tag{2.1}$$

where the operators $\hat{L}_k$ are system operators, commonly called the Lindblad operators, and the γ_k are specific dimension constants in order to make the $\hat{L}_k$ dimensionless.

In this scenario of weak coupling, a system in a nonequilibrium dynamics must obey the Kubo-Martin-Schwinger (KMS) stability criterion for thermal equilibrium [58, 59], where the transport coefficients (recalling, e.g., the transport equation of kinetic theory) are put in terms of equilibrium time correlation functions[1]. KMS condition implies that, at equilibrium,

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[1]These functions, also called Green functions, were first introduced by R. Kubo [58] in an attempt of

there is no heat flux between the system and bath.

Established the thermal equilibrium condition (the details behind the KMS condition are awfully complex and, hence, out of the scope of this dissertation), the zeroth follows straight-forward. Just consider a network of baths $(B_a, B_b, ...)$ connected by systems $(S_1, S_2, ...)$, for simplicity we take only three of each such that, in the *weak coupling limit* (WCL), we have

$$\hat{\rho} \approx \hat{\rho}_{s_1} \otimes \hat{\rho}_{s_2} \otimes \hat{\rho}_{s_3} \otimes \hat{\rho}_{b_a} \otimes \hat{\rho}_{b_b} \otimes \hat{\rho}_{b_c}, \tag{2.2}$$

and the hamiltonian

$$\begin{aligned} \hat{H} = \hat{H}_{s_1} + \hat{H}_{b_a} + \hat{H}_{s_1 b_a} + \hat{H}_{s_1 b_b} + \hat{H}_{s_1 b_c} + \hat{H}_{s_2} + \hat{H}_{b_b} + \hat{H}_{s_2 b_b} + \hat{H}_{s_2 b_a} + \hat{H}_{s_2 b_c} \\ + \hat{H}_{s_3} + \hat{H}_{b_c} + \hat{H}_{s_3 b_c} + \hat{H}_{s_3 b_a} + \hat{H}_{s_3 b_b}. \end{aligned} \tag{2.3}$$

Equation (2.2) states that there is no correlation between the systems and the baths, thus KMS condition establishes the thermal equilibrium between the system S_1 with the bath B_a, for example, and between the system S_2 with the bath B_b, so we can assign temperatures for them. Now if the systems S_1 and S_2 are also in thermal equilibrium with the bath B_c (which is the bath coupled to the system S_3), then S_1 is in thermal equilibrium with S_2 and we have obtained the zeroth law of quantum thermodynamics.

System-bath strong coupling

Apart from the WCL, we can have a situation with the system and the heat bath strongly interacting in such a way that the approximation (2.2) is no longer valid, thus the system and the bath are entangled and the system's internal energy must contain the interaction energy. First of all, there is no universal definition for temperature that is independent of the specific features of the body, despite it is quite easy to establish the temperature of any equilibrium state (exceptional cases like systems with negative heat capacity being the exception), this is not the case of a nonequilibrium state.

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generalizing quantum statistical mechanics to treat irreversible processes.

As we have previously seen, a nonequilibrium evolution of a system weakly coupled to a thermal bath obeys the KMS stability criterion and at the end of this evolution process, the system will be in thermal equilibrium with the bath and its temperature will be exactly the temperature of the bath. When we have a strong coupling between the system and the bath, things got a little bit complicated. We may still establish a thermal equilibrium condition, but the notion of temperature is lost and we have to resort to defining *effective temperatures*, which is not always possible.

As a special case, there is a recent result [60] about Gaussian quantum open systems strongly coupled to a heat bath, where a definition of nonequilibrium free energy is proposed and, with it, a time-varying effective temperature T^*. A Gaussian state [61] can be defined by a bosonic system if its Wigner function [62, 63] is Gaussian, or, equivalently, if its Husimi-Q function [64, 65] is a Gaussian function of the coherent state variables[2]. Putting the complications behind the theory of Gaussian states aside, beyond the definition of an effective temperature for such systems, it was shown that the effective temperature T^*, after the equilibration[3] with a heat bath, is slightly higher than the bath temperature T_B depending on the strength of the coupling. Thus, if a second Gaussian system is put into contact within the exact same heat bath until it reaches the equilibrium, the effective temperature may not be the same as T^*. This is the fundamental result that Hsiang and Hu [10] brought us, the zeroth law in the strong coupling limit can only be valid if we state the transitivity relation only within the framework of equilibrium (again, not *thermal* equilibrium) conditions, equilibrium is not the same as equal temperatures. Therefore, for strong coupling thermodynamics, the zeroth law of thermodynamics is established in terms of equilibrium between the bodies, but they are not necessarily with the same temperature.

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[2]The Husimi-Q function is the Weierstrass transform [66] of the Wigner function.

[3]Note that we are being very careful in distinguishing *equilibrium* from *thermal equilibrium*, thermalization demands more than equilibration, a system thermalized assume the canonical distribution form for the reduced density matrix, this would be our case if the coupling constant is small enough.

2.1.2 The I-Law

The first law of quantum thermodynamics is, like its classical counterpart, a statement about the conservation of energy and how it is transformed into heat or work during local changes in the system, which are the only two forms of energy transfer if there is no matter exchange with the environment. For the case of an unitary dynamics, there are two main different ways to approach the first law of quantum thermodynamics: from the classical definition of work and from the classical definition of heat.

Classical work approach

Let us consider the working substance as an arbitrary quantum system with a discrete energy spectrum, although is possible to generalize it to the infinite number of energy levels case [11]. The Hamiltonian of the working substance will be

$$\hat{H} = \hat{H} \underbrace{\left(\sum_n |n\rangle \langle n| \right)}_{\hat{\mathbb{I}}} = \sum_n \hat{H} |n\rangle \langle n| = \sum_n E_n |n\rangle \langle n| , \qquad (2.4)$$

where $|n\rangle$ is the nth energy eigenstate corresponding to the eigenenergy E_n. To obtain the internal energy U of the system, we need an average over the Hamiltonian

$$U \equiv \langle \hat{H} \rangle = tr\{\hat{\rho}\hat{H}\} = \sum_n \langle n| \hat{\rho}\hat{H} |n\rangle = \sum_n P_n E_n, \qquad (2.5)$$

with $P_n = \langle n| \hat{\rho} |n\rangle$ being the occupation probability of the corresponding energy level E_n and $\hat{\rho}$ is the system's density operator. Note that, and this is important, we have chosen the energy eigenstate basis $\{|n\rangle\}$ when calculating the trace operation. If we differentiate the previous equation, we get

$$dU = \sum_n (E_n dP_n + P_n dE_n). \qquad (2.6)$$

Recalling equation (1.1), to know, $dU = \dj Q + \dj W$, our first reaction is to compare it with equation (2.6) and find the associations for $\dj Q$ and $\dj W$. Following the classical concept of work, which is associated with modifications in generalized coordinates, which in turn

is associated with the change in the energy spectrum E_n in quantum mechanics, we must assign the work as

$$\dbar W = \sum_n P_n dE_n, \tag{2.7}$$

then, it follows that

$$\dbar Q = \sum_n E_n dP_n. \tag{2.8}$$

Classical heat approach

Now we are interested in approaching the I-law in a different perspective, we still keep our system with a discrete energy spectrum, however, instead of expanding the internal energy in the eigenenergy basis, we choose the eigenstate basis of the density operator $\{|k\rangle\}$. Then, in this scenario, we have

$$U \equiv \langle \hat{H} \rangle = tr\{\hat{\rho}\hat{H}\} = \sum_k \langle k| \hat{\rho}\hat{H} |k\rangle = \sum_k \rho_k \epsilon_k, \tag{2.9}$$

where $\rho_k = \langle k| \hat{\rho} |k\rangle$ and $\epsilon_k = \langle k| \hat{H} |k\rangle$ is the kth diagonal element of $\hat{H}$ in the $\{|k\rangle\}$ basis. Differentiating the previous equation, we obtain

$$dU = \sum_k [\epsilon_k d\rho_k + \rho_k d\epsilon_k]. \tag{2.10}$$

Recalling the von Neumann entropy $S = -k_B tr\{\hat{\rho}log\hat{\rho}\} = -k_B \sum_k \rho_k log\rho_k$, if we differentiate it, we obtain

$$dS = -k_B \sum_k [log\rho_k d\rho_k + d\rho_k] = -k_B \sum_k [log\rho_k d\rho_k], \tag{2.11}$$

where we have used the trace-preserving property $\sum_k \rho_k = 1$, which leads to $\sum_k d\rho_k = 0$. Now we are able to invoke the classical definition of heat, which states that heat corresponds to a change in the internal energy accompanied by a change in the entropy of the system. Therefore, equations (2.10) and (2.11) leads us to identify heat as

$$\dbar Q = \sum_k \epsilon_k d\rho_k, \tag{2.12}$$

and, consequently,

$$\text{d}\mathcal{W} = \sum_k \rho_k d\epsilon_k. \tag{2.13}$$

Reformulating the I-law

We have shown two different ways to approach the I-law, but are they consistent with each other? Well, we have used two different eigenstate basis to obtain the expressions for the heat and work, it is straightforward that we could simply take any pair of these equations and perform a change of basis to see the equivalence (or not) of both formalisms. Let us first start with equation (2.12) and rewrite it as the following

$$\text{d}\mathcal{Q} = \sum_k \epsilon_k d\rho_k = \sum_k \langle k| \hat{H} |k\rangle \, d\rho_k = \sum_k \langle k| \hat{H} \Big[\sum_n |n\rangle \langle n| \Big] |k\rangle \, d\rho_k$$

$$= \sum_k \langle k| \Big[\sum_n E_n |n\rangle \langle n| \Big] |k\rangle \, d\rho_k,$$

where we have used the completeness relation $\hat{\mathbb{I}} = \sum_n |n\rangle \langle n|$. If we define $c_{n,k} = \langle n|k\rangle$, then we can write

$$\text{d}\mathcal{Q} = \sum_{k,n} E_n |c_{n,k}|^2 d\rho_k. \tag{2.14}$$

On the other hand, if we start with equation (2.8), we obtain

$$\text{d}Q = \sum_n E_n dP_n = \sum_n E_n d(\langle n| \hat{\rho} |n\rangle) = \sum_n E_n d(\langle n| \hat{\rho} \Big[\sum_k |k\rangle \langle k| \Big] |n\rangle)$$

$$= \sum_n E_n d(\langle n| \Big[\sum_k \rho_k |k\rangle \langle k| \Big] |n\rangle) = \sum_n E_n d\Big(\sum_k \rho_k |c_{n,k}|^2 \Big)$$

$$= \sum_{n,k} E_n |c_{n,k}|^2 d\rho_k + \sum_{n,k} E_n \rho_k d[|c_{n,k}|^2],$$

or simply, using equation (2.14),

$$\text{d}Q = \text{d}\mathcal{Q} + \text{d}\mathcal{C}, \tag{2.15}$$

where we define the quantity $\text{d}\mathcal{C}$ as

$$\text{d}\mathcal{C} = \sum_{n,k} E_n \rho_k d[|c_{n,k}|^2]. \tag{2.16}$$

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If we do this very same analysis for the work in equations (2.7) and (2.13), we obtain

$$đ\mathcal{W} = đW + đ\mathcal{C}. \tag{2.17}$$

Equations (2.15) and (2.17) answer our question, both formalisms are equivalent only if the quantity $đ\mathcal{C}$ that we have defined is zero, i.e., if the coefficients $c_{n,k}$ are constants. After all, the quantity $đ\mathcal{C}$ is present in both expressions for heat and work, but what is its nature? Is the addition of extra heat into the system? Is it a realization of extra work into the system?

Well, our first thought is that it can not be both (work and heat) at the same time, so it must be neither of them. Equation (2.16) also shows us that $đ\mathcal{C}$ does not depend directly on dE_n or $d\rho_k$, so, again, it confirms our hypothesis that it can not be work or heat. This quantity depends on the variation of the quantity $|c_{n,k}|^2 = |\langle n|k\rangle|^2$, associated with the projection of the vectors of the $\{|k\rangle\}$ basis in the vectors of the $\{|n\rangle\}$ basis, and such a variation occurs if the *quantum coherence* of the system also varies, but in time [67, 68]. Thus, $\mathcal{C}(t)$ is the quantity that describes the quantum coherence of the system and can be explicitly calculated if we integrate in time the equation (2.16):

$$\mathcal{C}(t) = \sum_{n,k} \int_0^t (E_n\rho_k) \frac{d}{dt'} |c_{n,k}|^2 dt'. \tag{2.18}$$

This is a remarkable result obtained by Bertúlio [9], where he then propose since there is no classical analog for the quantum coherence, a redefinition of the first law of quantum thermodynamics as

$$dU = đW + đQ + đ\mathcal{C}, \tag{2.19}$$

where the coherence is recognized as a source, in the same level as work and heat, of the variation of internal energy of the system. Note that if we use the equations (2.15) and (2.17) to write dU in terms of $đ\mathcal{Q}$ and $đ\mathcal{W}$, the I-law would still be written in the same form $(dU = đ\mathcal{W} + đ\mathcal{Q} + đ\mathcal{C})$.

The I-law in the Markovian dynamics regime

Beyond the regime of an unitary dynamics, we can let the system interact with the bath in such a way that there is an entropy increase, but without leaving the weak coupling regime. Also, at this point, we restrict ourselves to a Markovian dynamics.

If we recall the evolution of an arbitrary operator $\hat{A}$, in the Heisenberg picture, we have

$$\frac{d}{dt}\hat{A} = \frac{i}{\hbar}[\hat{H}_S, \hat{A}] + \sum_j \left(\hat{V}_j \hat{A} \hat{V}_j^\dagger - \frac{1}{2}\{\hat{V}_j \hat{V}_j^\dagger, \hat{A}\} \right) + \frac{\partial \hat{A}}{\partial t}, \tag{2.20}$$

with $\hat{V}_j$ as system operators and $\hat{H}_S$ the hamiltonian of the system. In order to obtain the I-law of quantum thermodynamics, we will insert the system hamiltonian, $\hat{H}_S$, in the previous equation, obtaining

$$\frac{d}{dt}\hat{H}_S = \frac{i}{\hbar}[\hat{H}_S, \hat{H}_S] + \sum_j \left(\hat{V}_j \hat{H}_S \hat{V}_j^\dagger - \frac{1}{2}\{\hat{V}_j \hat{V}_j^\dagger, \hat{H}_S\} \right) + \frac{\partial \hat{H}_S}{\partial t}.$$

Taking the expectation value and noticing that the commutator of any operator with itself is zero, we have the following

$$\frac{d}{dt}\langle \hat{H}_S \rangle = \left\langle \sum_j \left(\hat{V}_j \hat{H}_S \hat{V}_j^\dagger - \frac{1}{2}\{\hat{V}_j \hat{V}_j^\dagger, \hat{H}_S\} \right) + \frac{\partial \hat{H}_S}{\partial t} \right\rangle,$$

or, using the linearity of the trace (remember that $\langle \hat{A} \rangle = tr[\hat{\rho}_S(t)\hat{A}]$),

$$\frac{dE_S}{dt} = \sum_j \left\langle \hat{V}_j \hat{H}_S \hat{V}_j^\dagger - \frac{1}{2}\{\hat{V}_j \hat{V}_j^\dagger, \hat{H}_S\} \right\rangle + \left\langle \frac{\partial \hat{H}_S}{\partial t} \right\rangle, \tag{2.21}$$

where E_S is the system's internal energy. Equation (2.21) illustrate the dynamics of the system, we know from the first law of thermodynamics that a change in the internal energy is only associated with an exchange of heat and work between the system and the environment[4], but in contrast to $dU = đQ + đW$, we have a derivative of the internal energy in time, so

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[4]We are here purposefully leaving aside the discussion about the role of coherence in the first law, mostly because there are no studies about the subject for Markovian dynamics in the same manner as we early elucidate it.

instead of heat and work, we will have heat currents $\mathcal{J}_j$ and power $\mathcal{P}$:

$$\frac{dE_S}{dt} = \sum_j \mathcal{J}_j + \mathcal{P}, \tag{2.22}$$

with the identifications

$$\mathcal{J}_j = \left\langle \hat{V}_j \hat{H}_S \hat{V}_j^\dagger - \frac{1}{2}\{\hat{V}_j \hat{V}_j^\dagger, \hat{H}_S\} \right\rangle, \tag{2.23}$$

and

$$\mathcal{P} = \left\langle \frac{\partial \hat{H}_S}{\partial t} \right\rangle. \tag{2.24}$$

Equations (2.23) and (2.24) represent the dynamical version of the first law of quantum thermodynamics in the Markovian regime. The problem behind using only LGKS generators (equation 2.1) lies in the fact that they are not unique, there is some arbitrariness of accounting for the system bath interaction energy in $\hat{H}_S$. In order to solve this non-uniqueness problem, some extra restrictions must be imposed for the dynamics generator, which is, again, not in the scope of this dissertation (see Ref.[55]).

2.1.3 The II-Law

The second law of thermodynamics is a statement about the irreversibility of some processes in nature, it is related to the time-reversal symmetry breaking. This is a very curious property in thermodynamics because the majority of the most important physical theories have time-reversal symmetry. Trying to enunciate the II-law of thermodynamics in the quantum regime can be a very tough task, as we will be seeing next.

Equilibrium states

We first start with a discussion about the II-law in equilibrium states for quantum systems. A *passive state* is defined as a state $\hat{\rho}$ that satisfies

$$tr(\hat{\rho}\hat{H}) \leq tr(\hat{U}\hat{\rho}\hat{U}^\dagger\hat{H}), \tag{2.25}$$

where $\hat{U}$ is an arbitrary unitary operator. In quantum mechanics, a reversible dynamics is directly related to unitary maps, thus, requiring the dynamics operator $\hat{U}$ to be unitary is a requirement for the evolution to be reversible. An example of a passive state is the Gibbs state, which corresponds to a state in thermal equilibrium with a heat bath at a fixed temperature.

The inequality (2.25) is telling us that the internal energy (remember that $\langle \hat{H} \rangle = tr(\hat{\rho}\hat{H})$) of the equilibrium state, represented by the passive state $\hat{\rho}$, can only increase and, therefore, that no work can be extracted from the system by such procedure. This is a quantum analog of Kelvin's statement of the II-law, in which it says that no work can be extracted from a single heat source at a fixed temperature in a cyclic process. Therefore, we can enunciate the II-law of quantum thermodynamics: *Starting with a passive state, no energy can be extracted by any unitary map.*

The role of entropy

In classical thermodynamics, the entropy S is a state function associated with a concrete process in which, for a closed system, can never decrease ($\Delta S \geq 0$), and by a concrete process we mean that the increase in entropy is inherent to the process, it is independent on how we see or measure it.

In contrast, in quantum mechanics we do not have a single universal definition for entropy as it was in classical thermodynamics, the entropy will depend on how we measure the system and how much information we may gather from this measurement. The entropy of an observable $\hat{O}$, with spectral decomposition $\hat{O} = \sum_k \alpha_k |\alpha_k\rangle \langle\alpha_k|$, is the Shannon entropy with respect to the possible outcomes

$$S_O = -\sum_k p_k \ln p_k, \tag{2.26}$$

where $p_k = tr(\hat{\rho}\hat{P}_k)$ is the probability of measuring α_k, $\hat{\rho}$ is the system's density operator that we are measuring and $\hat{P}_k = |\alpha_k\rangle \langle\alpha_k|$ is the projector over $|\alpha_k\rangle$ state. Note that we

have settled dimensionless units for the entropy (simply taking $k_B = 1$). Nonetheless, if there is such a variety of entropies depending on how much gathered information we may acquire from a measurement, there must be an optimal observable that maximizes the total information gathered and, therefore, minimizes its entropy. The entropy of this optimal observable is termed the von Neumann entropy S_{vn} and is given by

$$S_{vn} = -tr\{\hat{\rho} \ln \hat{\rho}\}. \tag{2.27}$$

Note that S_{vn} is a function of the eigenvalues of $\hat{\rho}$, this means that any unitary evolution acting on $\hat{\rho}$ will not change the von Neumann entropy, $S_{vn}(\hat{U}\hat{\rho}\hat{U}^\dagger) = S_{vn}(\hat{\rho})$, because unitary transformations does not affect the eigenvalues of $\hat{\rho}$. Hereupon, the reversible dynamics of the unitary evolution maps can not increase or decrease the (von Neumann) entropy of the system, this is in line with the original concept of entropy in classical thermodynamics.

Another feature of the classical concept of entropy is that it is additive, the entropy of a system is the sum of the entropies of its subsystems. However, entropy in quantum mechanics is not additive unless the system state is composed by a tensor product of its subsystems, $\hat{\rho} = \prod_j \otimes \hat{\rho}_j$, which, in general, is not the case, the subsystems may be entangled and when this happens, the sum of the entropies of the subdivisions are greater than the total von Neumann entropy. As an example, we know that the entropy of a pure state is zero because there is no uncertainty in this state, but if this pure state is composed by subdivisions entangled, then it is easy to see that the sum of the entropies associated with the local measurements in the subdivisions is greater than zero.

Non-equilibrium states

In the context of classical thermodynamics, entropy is a function of equilibrium, it can not be well defined for a system experiencing non-equilibrium dynamics, we may only calculate the entropy immediately before and after the non-equilibrium evolution and, in this way,

calculate how much of entropy was produced[5]. However, the entropy production for a closed system can be negative, mathematically speaking there is a finite possibility for it to occur, but this does not violate the II-law because, physically speaking, this possibility is absurdly improbable, and the average entropy production is always nonnegative.

The fluctuating theorems bring us new insights into the entropy production under non-equilibrium dynamics. Therefore, the second law of thermodynamics must be reformulated in terms of these fluctuating theorems that started the field of stochastic thermodynamics [70, 71], these theorems can also be naturally translated into the quantum regime [72, 73].

2.1.4 The III-Law

There are two formulations for the third law of thermodynamics, both of them were originally stated by Walther Nernst during the years 1906-12. The first one is the Nernst heat theorem, which states that the entropy of any pure substance in thermodynamics equilibrium goes to zero as the temperature approaches zero. The second one is the unattainability principle, which states that it is impossible by any procedure to cool any system to absolute zero temperature in a finite number of operations. In contrast to the Nernst heat theorem, which is a formulation of the third law in a purely static regime (equilibrium), the unattainability principle is a dynamical version for the third law, which is a more restrictive formulation that imposes limitations on the interaction between the system and bath.

Trying to enunciate the third law of thermodynamics in the context of quantum open systems is, as usual, not an easy task and it is still an active source of discussions. Levy and collaborators [74] demonstrated the unattainability principle in the context of quantum refrigerators and Ref. [75] do the same thing using quantum resource theory [76], but Ref. [77] criticize this principle and claims proof of its violation, stating that only Nernst heat

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[5]It turns out that in nonequilibrium statistical mechanics it is possible, for example, to define an entropy function for a finite classical system in a nonequilibrium steady state [69], where steady state means that the properties of the system are independent of time.

theorem is a valid formulation for the third law in the quantum regime, which is also proved to be valid for quantum oscillators with various types of heat baths [78, 79]. Ref. [79] also rebuts some early claims of violations in the laws of quantum thermodynamics.

Nevertheless, in a 2013 review of quantum thermodynamics [4], Kosloff advocates that the laws of thermodynamics are true in any quantum circumstance and that any apparent violation of them should be viewed with skepticism because, despite the endless attempts, there is no successfully rebut of them and most of these apparent violations are caused by flaws in the approximations taken, usually in the derivation of the master equations. Specifically for the third law, in a 2019 paper [7], Shastry defends the ideas brought by Kosloff and presents proof of the Nernst heat theorem for generic open quantum systems of independent fermions, both in and out of equilibrium, with strong coupling to reservoirs.

2.2   Quantum thermal machines

We have already shown in section (1.1) how the thermal machines are constructed from the classical thermodynamics point of view. Now, how can we properly define a quantum heat engine (QHE)? A simplistic answer is that a QHE is a machine that converts heat into useful work using a quantum system as its working substance. The number of possibilities for models of QHEs has no limits since we can, in principle, use any quantum system as the working substance, nevertheless, we can broadly classify them as reciprocating or continuous.

Reciprocating engines, or even *discrete engines*, are the ones where the cycle operation is composed by a series of strokes where the system is coupled or decoupled from thermal baths in each stroke [11, 80]. Therefore, a reciprocating engine is defined as the product of quantum operations that acts on the working substance's density operator $\hat{\rho}$:

$$\hat{\mathcal{U}}_{cyc} = \prod_j \hat{\mathcal{U}}_j, \tag{2.28}$$

with $\hat{\mathcal{U}}_{cyc}$ being the cycle propagator and $\hat{\mathcal{U}}_j$ are stroke propagators. Quantum operations are

defined as completely positive and trace preserving maps on the space of density matrices, they map positive elements into positive elements without changing the value of the trace of the density operator. Kraus' theorem ensures that if Λ is a quantum operation then

$$\Lambda \hat{\rho} = \sum_j \hat{W}_j^\dagger \hat{\rho} \hat{W}_j, \tag{2.29}$$

where $\hat{W}_j$ are operators (also called *Kraus operators*) satisfying $\sum_j \hat{W}_j^\dagger \hat{W}_j = \mathbb{I}$. Similar to the thermalization process of a system in contact with a heat reservoir, a reciprocating engine will, after the required time, settles to a steady state regime called the *limit cycle* [81]. The steady state operation is an invariant of the cycle propagator $\hat{\mathcal{U}}_{cyc} \hat{\rho}_{st} = \hat{\rho}_{st}$ and if $\hat{\mathcal{U}}_{cyc}$ have a single non-degenerate invariant state, then we call $\hat{\rho}_{st}$ the limit cycle $\hat{\rho}_{lc}$ instead. Thus, if $\hat{\rho}_{lc}$ is proved to exist then any arbitrary initial state will approach it if the cycle is repeatedly applied.

In contrast, *continuous engines* are the ones where the system is coupled to the thermal baths during the whole cycle of operation of the engine, this way attaining a steady-state operation [82]. Unlike the reciprocating engines, continuous engines do not present a limit cycle where the state of the quantum system is the same at the end of each cycle, they operate in a constant steady state regime $\hat{\rho}_{st}$, where the properties of the system are independent of time.

There are two different classifications for the continuous engines, they can be autonomous or driven. Continuous autonomous engines [83, 84] operate without any external time-dependent driving, but they are coupled with three or more thermal baths simultaneously. The tricycle model [85] is the template for almost all continuous engines, which consists of three thermal baths: a hot bath with temperature T_h, a cold bath with temperature T_c, and a work bath with temperature T_w. The device operates as an engine by either heating the hottest bath or cooling the coldest bath, and it can also be viewed as a heat transistor [86]. On the other hand, a continuous driven engine operates with an external intervention, i.e., the device is connected to an external power source to reach steady state and regulate its

operation [87].

2.2.1   Unitary dynamics of quantum thermodynamic cycles

In order to construct a quantum Carnot engine (QCE) or a quantum Otto engine (QOE), first, we need to define what is the corresponding quantum versions of the thermodynamic processes.

Quantum thermodynamic processes in an unitary dynamics

Assuming a quasistatic unitary dynamics and recalling the I-law in the classical work approach (equations 2.7 and 2.8), we may start with the corresponding quantum version of the isothermal process. We know that the main feature of this process is to keep the temperature of the working substance constant so that the system is all the time in thermal equilibrium with the heat bath. At first sight, we do not have a clear universal assignment of temperature for a quantum system, but if this quantum system is in thermal equilibrium with a heat bath, then we may induce the temperature of the system as the same as the temperature of the heat reservoir (otherwise there would be a heat flux between the system and the reservoir and, consequently, there would be no thermal equilibrium). Therefore, in a *quantum isothermal process* work can be done and, at the same time, heat can be absorbed, in such a way that both the eigenenergies E_n and the occupation probabilities P_n changes simultaneously and the thermodynamic equilibrium condition is achieved at every instant. This leads the density operator to assume thermally distributed populations in the quantum states $|n\rangle$:

$$\hat{\rho}(t) = (1/Z) \sum_n exp[-E_n(t)/(k_B T)] |n(t)\rangle \langle n(t)| \tag{2.30}$$

with k_B being the Boltzmann constant and $Z = \sum_n exp[-E_n(t)/(k_B T)]$ the canonical partition function. Also, Ref. [11] uses some counterexamples to show that the internal energy of the system changes during the quantum isothermal processes, unlike its classical counterpart

for an ideal gas.

On the other hand, a *quantum isochoric process* can also be defined taking its classical counterpart to compare. In a classical isochoric process, there is no variation in the volume of the system and, consequently, no work is done. To achieve this feature in our quantum analog, it is enough to assume, evoking equation (2.7), that there is no variation in the eigenenergies, $dE_n = 0$. Thus, to realize a quantum isochoric process, we need to put our working substance into contact with a heat bath, this way the system can exchange heat until the system reaches thermal equilibrium with the heat bath, but, during this process, we are not allowed to let the eigenenergies change. In general, the Hamiltonian of the working substance is controlled by an external parameter that changes the energy scale, which makes this process easier to perform in an experiment.

Following the same reasoning, a *quantum adiabatic process* is defined as the one with no heat exchange $đQ = 0$ between the system and the heat bath, and, recalling equation (2.8), the population distribution of the system must remain unchanged, $dP_n = 0$. It is important to state that a quantum adiabatic process does not imply in a classical adiabatic process, if the process proceeds very fast, for example, there is no time for the heat to be exchanged classically, but internal excitations may occur and the occupation probabilities P_n will not remain unchanged. This is the reason a quantum adiabatic process needs to proceed very slow, although there are proposals of different ways to find a "shortcut" to the quantum adiabatic condition away from the quasistatic regime.

Quantum Carnot cycle

Just like in classical thermodynamics, the quantum Carnot cycle does not have much practical importance besides being the most efficient idealized machine. It establishes the upper limit for the efficiency of any thermal machine operating between two heat reservoirs. The QCE consists of two quantum isothermal processes ($A \rightarrow B$ and $C \rightarrow D$) and two quantum adiabatic processes ($B \rightarrow C$ and $D \rightarrow A$), and also must be operated reversibly.

Reversibility in quantum mechanics is associated with unitary evolution, but we are interested here in thermodynamic reversibility. Therefore no thermalization process is allowed, otherwise, entropy would increase the entropy of the working substance plus the bath and this cycle would be irreversible. For any isolated system presenting discrete energy levels, H.T. Quan [11] proves that this is achievable by changing all the energy gaps by the same ratio $E_n(B) - E_m(B) = \lambda[E_n(C) - E_m(C)]$ and $E_n(A) - E_m(A) = \lambda[E_n(D) - E_m(D)]$ $(n = 0, 1, 2...)$, with $\lambda = T_h/T_c$ and , T_h and T_c being the temperatures of the hot and the cold reservoirs, respectively.

We are interested in finding the efficiency η_C of the QCE. We could as well use equation (2.8) to calculate heat transferred during the quantum isothermal processes, but, for simplicity, we use the expression $dQ = TdS$, which is valid because the system is in thermal equilibrium during the whole process. Thus, the heat absorbed Q_h and released Q_c can be calculated as follows:

$$Q_h = \int_A^B T_h dS = T_h[S(B) - S(A)] > 0, \tag{2.31}$$

$$Q_c = \int_C^D T_c dS = T_c[S(D) - S(C)] < 0, \tag{2.32}$$

where the temperature is taken out of the integral because the temperature of the working substance is constant during the quantum isothermal expansion $(A \to B)$ and the quantum isothermal compression processes $(C \to D)$. The entropy of the working substance at the end of any of the processes (using the Boltzmann distribution for thermal equilibrium) is given by the time derivative of the Helmholtz free energy

$$S(i) = -\frac{\partial A(i)}{\partial T_i} = -\frac{\partial}{\partial T_i}[-\beta_i^{-1} \ln Z(i)] = k_B \ln Z(i) + \frac{k_B}{Z(i)} \sum_n \beta_i E_n(i) \exp[-\beta_i E_n(i)],$$

or simply,

$$S(i) = -k_B \sum_n \frac{\exp[-\beta_i E_n(i)]}{Z(i)}[-\beta_i E_n(i) - \ln Z(i)], \tag{2.33}$$

where $Z(i)$ and $E_n(i)$ are, respectively, the partition function and eigenenergies in the corresponding instants $i = A, B, C, D$. Here, $\beta_A = \beta_B = 1/k_B T_h$, $\beta_C = \beta_D = 1/k_B T_c$. The

work W_C of the QCE can be calculated using equations (2.31) and (2.32), and the first law of thermodynamics

$$W_C = Q_h + Q_c = (T_h - T_c)[S(B) - S(A)], \qquad (2.34)$$

where we have used the fact that $S(A) = S(D)$ and $S(B) = S(C)$, since $(A \to D)$ and $(B \to C)$ are quantum adiabatic processes (no generation of entropy is allowed). Note that, in order to extract positive work from the bath, it is sufficient to have $T_h > T_c$, which is the positive-work condition. Finally, the efficiency of the QCE is given by

$$\eta_C = \frac{W_C}{Q_h} = 1 - \frac{T_c}{T_h}, \qquad (2.35)$$

which is the same as the classical Carnot engine. Using the reversibility condition $E_n(B) - E_m(B) = (T_h/T_c)[E_n(C) - E_m(C)]$, we can write the efficiency in terms of the energy gaps:

$$\eta_C = 1 - \frac{E_n(C) - E_m(C)}{E_n(B) - E_m(B)}. \qquad (2.36)$$

Quantum Otto cycle

The Otto engine is one of the most widely used engines in operation nowadays, mostly present in automobiles. Its quantum version, the QOE, is maybe the most explored cycle in the later years, it consists of two quantum isochoric $(A \to B$ and $C \to D)$ and two quantum adiabatic processes $(B \to C$ and $D \to A)$. The heat absorbed, Q_h, and released, Q_c, by the working substance during the quantum isochorical processes is given by

$$Q_h = \sum_n \int_A^B E_n dP_n = \sum_n E_n^h[P_n(B) - P_n(A)], \qquad (2.37)$$

$$Q_c = \sum_n \int_C^D E_n dP_n = \sum_n E_n^c[P_n(D) - P_n(C)], \qquad (2.38)$$

where the eigenenergy is taken out of the integral since the eigenenergy of the working substance is constant during the quantum isochoric heating $(E_n = E_n^h$ in $A \to B)$ and the quantum isochoric cooling $(E_n = E_n^c$ in $C \to D)$. The work W_O of the QOE can be calculated

using the previous equations and the first law of thermodynamics

$$W_O = Q_h + Q_c = \sum_n (E_n^h - E_n^c)[P_n(B) - P_n(A)], \tag{2.39}$$

where we have used the fact that $P_n(B) = P_n(C)$ and $P_n(A) = P_n(D)$ since $(B \to C)$ and $(A \to D)$ are quantum adiabatic processes. The efficiency of the Otto cycle can be calculated as follows

$$\eta_O = \frac{W_O}{Q_h} = \frac{\sum_n (E_n^h - E_n^c)[P_n(B) - P_n(A)]}{\sum_n E_n^h [P_n(B) - P_n(A)]} = 1 - \frac{\sum_n E_n^c [P_n(B) - P_n(A)]}{\sum_n E_n^h [P_n(B) - P_n(A)]}. \tag{2.40}$$

2.2.2 Finite-time thermal machines

Real engines operate far from equilibrium conditions and in a finite time. Their performance is restricted by the rate of heat transport, friction and heat leaks. A dynamical viewpoint is therefore the next required step.

In this subsection, we focus on the dynamic version of the QOE, a *reciprocating engine*. As we stated before, the QOE is composed of four strokes: two *adiabats*, where the working medium is isolated from the environment and an external parameter ω that controls the energy scale of the working medium varies, and two *isochores*, where the working medium is in contact with a heat bath and the external control remains constant. In the *adiabats* no heat is exchanged and only work can be consumed or produced. In the *isochores* only heat is allowed to be exchanged between the working medium and the environment. The cycle is then described as the following:

(i) The compression *adiabat*: the external parameter increases from ω_c to $\omega_h > \omega_c$ in a time period τ_{ch} while the working medium is isolated from the environment. The stroke is described by the propagator $\hat{\mathcal{U}}_{ch}$.

(ii) The hot *isochore*: the external parameter ω_h remains constant while the working medium is coupled with a heat bath at temperature T_h during a time period τ_h exchanging heat. The stroke is described by the propagator $\hat{\mathcal{U}}_h$.

(iii) The expansion *adiabat*: the external parameter decreases from ω_h to ω_c in a time period τ_{hc} while the working medium is isolated from the environment. The stroke is described by the propagator $\hat{\mathcal{U}}_{hc}$.

(iv) The cold *isochore*: the external parameter ω_c remains constant while the working medium is coupled with a heat bath at temperature T_c during a time period τ_c exchanging heat. The stroke is described by the propagator $\hat{\mathcal{U}}_c$.

The cycle propagator is then described as the product of individual propagators (see equation 2.28)

$$\hat{\mathcal{U}}_{cyc} = \hat{\mathcal{U}}_c \hat{\mathcal{U}}_{hc} \hat{\mathcal{U}}_h \hat{\mathcal{U}}_{ch}. \tag{2.41}$$

The refrigerator cycle can easily be obtained by simply reversing the sequence of the propagators in equation (2.41), i.e.,

$$\hat{\mathcal{U}}_{cyc}^{ref} = \hat{\mathcal{U}}_{ch} \hat{\mathcal{U}}_h \hat{\mathcal{U}}_{hc} \hat{\mathcal{U}}_c. \tag{2.42}$$

To obtain a finite time allocated in the *adiabats*, the unitary strokes $\hat{\mathcal{U}}_{ch}$ and $\hat{\mathcal{U}}_{hc}$ must deviate from the adiabatic limit. This means that the rapid change in the energy scale of the working medium does not allow its state to follow adiabatically the instantaneous energy levels, coherence is then generated. But generating coherence requires a cost of additional external work, as a result, both coherences and additional energy become stored in the working medium. This additional energy will dissipate into the cold bath and the appearance of decoherence is inevitable, both phenomena are "nonadiabatic" effects, which are the quantum analog of friction that has been termed *quantum friction* [88, 89]. Although it seems contradictory to have "nonadiabatic" effects in the *adiabats*, here "nonadiabatic" is referred as in the quantum sense (recalling the quantum adiabatic theorem [90]) and *adiabat* as in the thermodynamic sense. There are two main strategies to shorten the time in the *adiabats*. One strategy is to find a frictionless protocol where the price of generating coherence is reduced, these protocols are termed shortcuts to adiabaticity [91–93]. The other strategy is to maintain the coherence during the cycle by shortening the cycle time [94].

For the engine to obtain a finite power output, the time in the *isochores* must also be shortened, i.e., the thermalization strokes $\hat{\mathcal{U}}_c$ and $\hat{\mathcal{U}}_c$ should be restricted. This is done by avoiding the infinite time full thermalization. It is shown that optimizing the power output at high temperature leads to [95]:

$$\eta_{ca} = 1 - \sqrt{\frac{T_c}{T_h}}, \tag{2.43}$$

which is the Curzon-Ahlborn efficiency. The original paper by Curzon and Ahlborn [29] obtained equation (2.43) for classical thermodynamics in the endoreversibility context and started the field of finite time thermodynamics, as we previously elucidated in the first chapter.

The Hamiltonian that describes our engine is constituted by three components

$$\hat{H}(\omega) = \hat{H}_0 + \hat{H}_{ext}(\omega) + \hat{H}_{int}, \tag{2.44}$$

where $\hat{H}_0$ is the free Hamiltonian, $\hat{H}_{ext}(\omega)$ is the external control Hamiltonian that brings the influence of the external time-dependent control field ω and $\hat{H}_{int}$ is the Hamiltonian that represents the internal interaction. The working medium consists of an ensemble of quantum systems and, together with the above Hamiltonian, is described by the density operator $\hat{\rho}$. In order to fully describe the QOE in this regime, we must establish the dynamic equations for the *adiabats* and the *isochores*.

Dynamics on the Adiabats

In the *adiabats* the working medium is isolated from the environment, thus the evolution of the density operator is given by the von Neumann equation:

$$\frac{d\hat{\rho}}{dt} = -i[\hat{H}(\omega), \hat{\rho}]. \tag{2.45}$$

The energy of the system is given by the average $\langle E \rangle = \text{Tr}\{\hat{H}(\omega)\hat{\rho}\}$ and its variation in time is

$$\frac{d}{dt}\langle E \rangle_a = \text{Tr}\left\{\left(\frac{d}{dt}\hat{H}(\omega)\right)\hat{\rho}\right\} + \text{Tr}\left\{\hat{H}(\omega)\frac{d\hat{\rho}}{dt}\right\}$$
$$= \text{Tr}\left\{\left(\frac{d}{dt}\hat{H}(\omega)\right)\hat{\rho}\right\} + \text{Tr}\left\{\hat{H}(\omega)\left(-i[\hat{H}(\omega),\hat{\rho}]\right)\right\},$$

where we have used the equation (2.45) and the linearity of the trace. Thus, using the cyclic property of the trace, the second term in the RHS of the previous equation vanishes and we get

$$\frac{d}{dt}\langle E \rangle_a = \text{Tr}\left\{\left(\frac{d}{dt}\hat{H}(\omega)\right)\hat{\rho}\right\}. \tag{2.46}$$

This is the change of the energy on the *adiabats* due to the explicit time dependence of ω. Since no heat is exchanged during the *adiabats*, the total change in the energy of the system must the work and, for a time period t, the total work done is obtained by simply integrating the rate of change of the energy

$$W(t) = \int_0^t \frac{d}{dt'}\langle E \rangle_a dt' = \langle E(t) \rangle_a - \langle E(0) \rangle_a. \tag{2.47}$$

The propagators $\hat{\mathcal{U}}_{ch}$ and $\hat{\mathcal{U}}_{hc}$ can be obtained from the density operator evolution (equation 2.45).

Dynamics on the Isochores

In the *isochores* the working medium is put in contact with a heat bath at temperature T_j while the external control field is kept constant ω_j, with $j = c, h$. If the working medium is weakly coupled to the bath, the thermalization process is described by the Lindblad master equation (cf. equation 2.1),

$$\frac{d\hat{\rho}}{dt} = -i[\hat{H}(\omega_j),\hat{\rho}] + \mathcal{L}_j(\hat{\rho}), \tag{2.48}$$

where

$$\mathcal{L}_j(\hat{\rho}) = \sum_k \gamma_k \left(\hat{L}_k\hat{\rho}\hat{L}_k^\dagger - \frac{1}{2}\{\hat{L}_k^\dagger\hat{L}_k,\hat{\rho}\}\right). \tag{2.49}$$

60

The Lindblad operators $\hat{L}_k$ are transition operators between neighboring energy levels of the Hamiltonian $\hat{H}$ and γ_k are the corresponding transition rates. The energy change in the system is given by

$$\frac{d}{dt}\langle E \rangle_i = \mathrm{Tr}\left\{ \left(\frac{d}{dt}\hat{H}(\omega_j) \right)\hat{\rho} \right\} + \mathrm{Tr}\left\{ \hat{H}(\omega_j)\frac{d\hat{\rho}}{dt} \right\}$$
$$= \mathrm{Tr}\left\{ \hat{H}(\omega_j)\left(-i[\hat{H}(\omega_j),\hat{\rho}] \right) \right\} + \mathrm{Tr}\left\{ \hat{H}(\omega_j)\mathcal{L}_j(\hat{\rho}) \right\},$$

where we have used the fact that on the isochores the Hamiltonian is independent of time. Using the cyclic property of the trace to eliminate the first term in the RHS of the previous equation, the energy change reduces to

$$\frac{d}{dt}\langle E \rangle_i = \mathrm{Tr}\left\{ \hat{H}(\omega_j)\mathcal{L}_j(\hat{\rho}) \right\}. \tag{2.50}$$

This is the change of the energy on the *isochores* due to the dissipation term $\mathcal{L}_j(\hat{\rho})$. Since this dissipation on the *isochores* must be exchanging heat, the total heat exchanged for a time period t is

$$Q_j(t) = \int_0^t \frac{d}{dt'}\langle E \rangle_a dt' = \langle E(t) \rangle_i - \langle E(0) \rangle_i. \tag{2.51}$$

The propagators $\hat{\mathcal{U}}_c$ and $\hat{\mathcal{U}}_h$ can be obtained from the density operator evolution (equation 2.48).

Quantum Lubrication

We did not mention before, when obtaining equations (2.46) and (2.50), but, a priori, quantum friction is present and energy is being lost. Therefore, following the ideas behind the *quantum lubrication* [15], we can add an external noise to the engine in order to suppress these frictional losses. This external noise is the pure dephasing, which is considered by adding into equations (2.45) and (2.48) the following term

$$\mathcal{L}_D(\hat{\rho}) = -\Lambda[\hat{H}(\omega),[\hat{H}(\omega),\hat{\rho}]]. \tag{2.52}$$

Note that the addition of this term does not change the results of energy change on the *adiabats* (equation 2.46) and *isochores* (equation 2.50), since the trace $\mathrm{Tr}\{\hat{H}(\omega)\mathcal{L}_D(\hat{\rho})\}$ vanishes.

Surpassing the Carnot efficiency bound

Some authors claim a supposed violation of the thermodynamic Carnot bound for the efficiency of a machine [96–98], but, in the same way as Kosloff criticizes the supposed violations of the laws of thermodynamics, these claims must be faced with skepticism. In general, these claims are associated with hybrid engines [99, 100], where the working medium is coupled with non-thermal baths and work can be delivered without any heat input. Due to these non-thermal baths, the efficiency bound does not solely follow the laws of thermodynamics. Therefore, it is reasonable to say that these hybrid engines cannot be compared to usual thermal machines, where the Carnot bound is established as a consequence of the second law. Despite all this, they do not violate any principle of thermodynamics [14, 101].

Chapter Three

Quantum dots

In this chapter, we give a brief introduction about the study of the *quantum dots* and its electronic transport properties to apply them in a new physical model for a quantum thermal machine in the next chapter. We start by defining the semiconductors heterostructures and then discuss the experimental implementation for confining electrons in *quantum wells*, *quantum wires* and, finally, *quantum dots*. We end the chapter with a description of artificial molecules, which are the *double quantum dots*.

3.1   Semiconductors heterostructures

Solids are an arrangement of atoms connected by chemical bonds and they can be broadly classified as *crystals* or *amorphous solids*. The *crystals* are characterized by a periodic regular structure for the distribution of atoms and molecules, and the *amorphous solids* are characterized by the lack of a definite lattice pattern, they have no periodicity and no definite form. The composition and arrangement of these structures determine the properties of the solids, such as density, malleability, hardness, optical transmission, conductivity, etc. Focusing on the conductivity property, we can classify the solids as metals (or conductors), semiconductors, or insulators.

In the metals, the conduction band and the valence band[1] overlap and electrons can

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[1]The electronic population of a solid is distributed in energy bands, the conduction, and valence band,
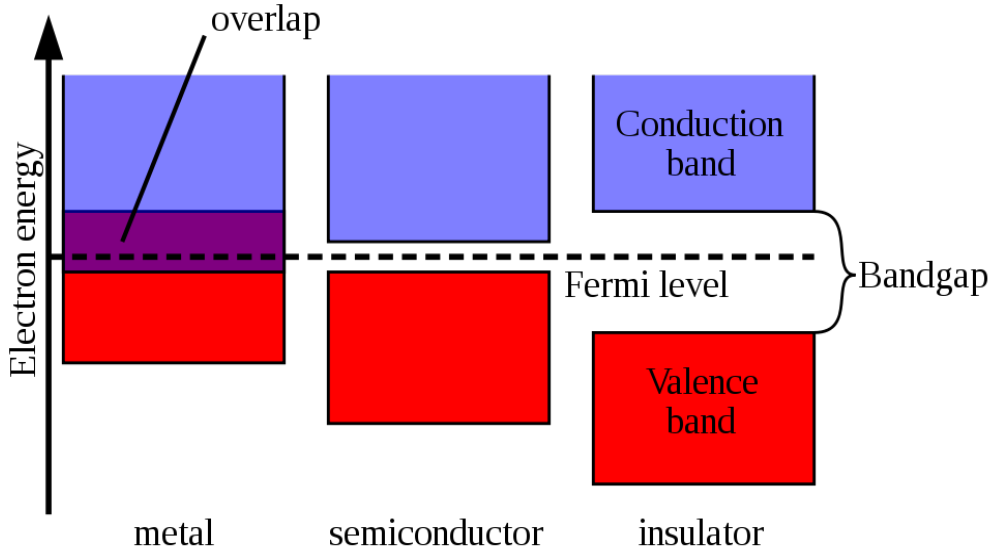
Figure 3.1 Energy bands for metals, semiconductors and insulators. The Fermi level is the name given to the highest energy occupied electron orbital at absolute zero temperature.

readily jump between the two bands, as we can see in figure 3.1. The insulators are characterized by a large bandgap, which means that the electrons have a large resistance in being excited to the conduction band. Nevertheless, our greater interest in this chapter is in the semiconductors, although the distinction between semiconductors and insulators is a matter of convention, a semiconductor is characterized by an intermediate-sized but non-zero band gap. Semiconductors can be pure elements, such as silicon (Si) or germanium (Ge), or compounds such as gallium arsenide (GaAs) or cadmium selenide (CdSe).

First proposed in 1970 by L. Esaki and R. Tsu [102], the fabrication of hybrid structures composed of thin layers of different interleaved semiconductors was only realized experimentally in 1974 with the works of L. Esaki, L. L. Chang, R. Dingle and co-workers [103–105]. These hybrid structures are termed as *semiconductors heterostructures*. The intercalation of layers of different semiconductors with nanometric thickness generates the quantization for

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separated by a forbidden region where the electrons cannot occupy. This forbidden region is the energy gap, or simply the bandgap. For an electron to jump from the valence band into the conduction band, it must be thermally excited with an energy of, at least, the energy gap.
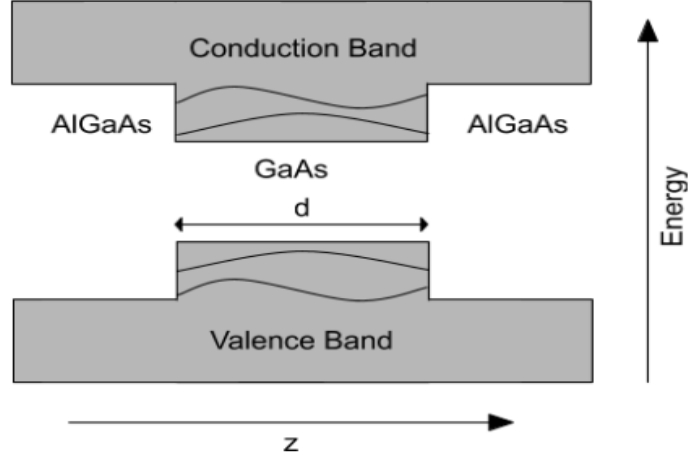
Figure 3.2 The band structure diagram in a quantum well of GaAs in between AlGaAs. The AlGaAs is used because it has very nearly the same lattice constant as GaAs, but a larger bandgap.

the movement of electrons in the structure. As an example consider the quantum wells, they can be made with heterostructures as the following: a layer of a semiconductor is placed between two layers of a different semiconductor with a higher energy gap, this way an electron in the conduction band or a hole in the valence band can be confined in the potential well created in the structure (see figure 3.2). Therefore, the quantization appears as a direct consequence of the confinement.

The confinement in a single direction generates the quantum wells, but further directions can also be restricted. *Quantum wires* appears with the confinement of electrons in two directions, which makes them quasi-one-dimensional systems (their width ω must be comparable to the Fermi wavelength). The electronic transport in these quantum wires can be classified in two different regimes: diffusive regime and ballistic regime. Being L the length of the wire and l_e the elastic mean free path, we have the following description of the regimes:

- *Diffusive regime* $(L \gg l_e)$: The length of the wire is long enough for the electrons to suffer many elastic scattering during their trip along the wire (figure 3.3(a)).

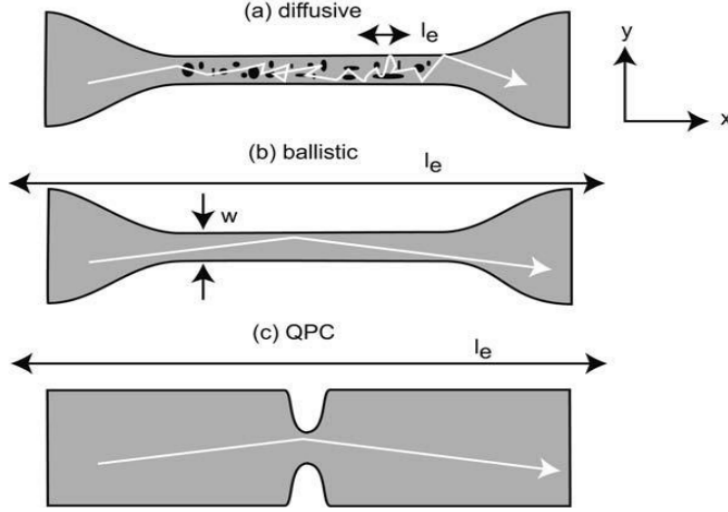- *Ballistic regime* $(L < l_e)$: The length of the wire is short enough for the electrons to

Figure 3.3 (a) Illustration of a diffusive wire, where the elastic mean free path l_e is much shorter than the length L of the wire, what causes many scattering events. (b) Illustration of a ballistic wire, where $l_e < L$ and the only scattering occurs in the confining walls. (c) Illustration of a quantum point contact (QPC), which is a ballistic wire with $\omega \approx L \ll l_e$. Figure adapted from Ref. [106].

move freely, without any elastic scattering, along the wire, except for the boundary scattering at the walls (figure 3.3(b)).

For ballistic wires, if their length are short enough to form a point-like contact between the left and right reservoirs ($\omega \approx L \ll l_e$), we call them *quantum point contacts* (QPCs), see figure 3.3(c). The QPC is the simplest mesoscopic system there is and classically we could expect for it an infinite conductance since there is no scattering, but surprisingly, in the low temperature regime, it has a quantized resistance for the electronic transport, i.e. its conductance G is quantized in units of $G_0 = 2e^2/h$ [106, 107].

Going further, we may confine the electrons in all of the three directions, we observe then the formation of a conducting island where electrons are trapped in a very small region of a size comparable to the Fermi wavelength; we call it a *quantum dot* [18].
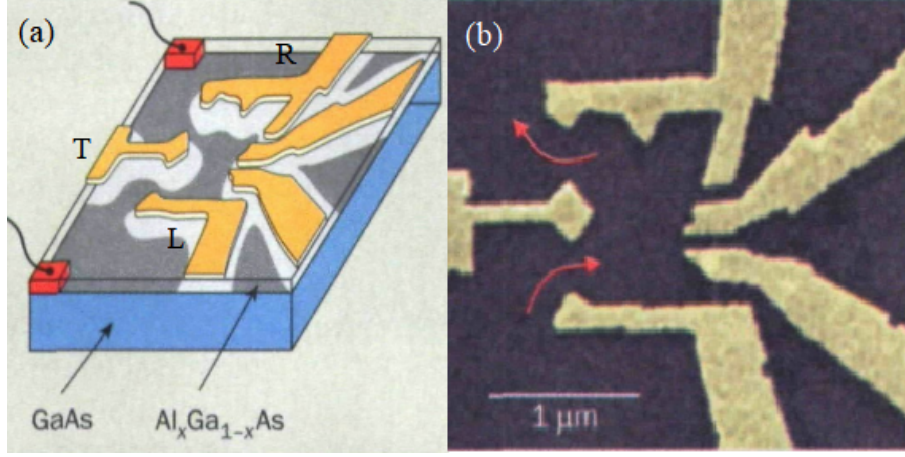
Figure 3.4 (a) Illustration of a quantum dot in the two-dimensional interface between gallium arsenide (GaAs) and aluminium gallium arsenide ($Al_xGa_{1-x}As$, with $x \approx 7\%$). (b) Electron microscopy of the quantum dot illustrated in (a). Both figures were adapted from Ref. [108].

3.2   Quantum dots

A quantum dot is a semiconductor particle and it is sometimes called an artificial atom because of its similarities with a real one. The differences between them are essentially their size (0.1nm for atoms against $\approx$ 100nm for quantum dots), and the shape and strength of the confining potential. Exactly as real atoms, the quantum dots admit a discrete energy spectrum and can only retain a finite number of electrons. In order to change the number of electrons in an atom, we can ionize it, however, in quantum dots, the number of electrons can also be adjusted by simply tuning the confinement potential. This way we can scan through the entire periodic table by simply changing a voltage.

A lateral quantum dot is made by trapping electrons at the interface between semiconductors heterostructures, forming this way a two-dimensional electron gas (2DEG) in this interface. The confinement in the other two directions is generated by voltages in electrodes formed at the interface layer. Figure 3.4 illustrates a quantum dot for a GaAs/AlGaAs heterostructure with gold electrodes (in yellow), the gate pairs T-L and T-R form two quantum point contacts (QPCs) that can be tuned in the tunneling regime (the conductance of both

QPCs is reduced below $2e^2/h$) and a closed quantum dot is formed. Electrons coming from a source can pass in and out of the dot through the two tunneling barriers (red arrows on figure 3.4(b)) and then reaches a drain (both source and drain are illustrated as red rectangular boxes), but a depletion region around the gates prevents them from passing through the other gaps.

For electrons from the source to enter the quantum dot, they must face a potential barrier and can only surpass it through the quantum tunneling effect. However, the discrete unit of charge on an electron generates a genuinely classic effect, mainly caused by Coulomb repulsion. If we have relatively high potential barriers separating the dot from the source and drain, the tunneling to the dot is weak and the number of electrons on the dot is fixed. Therefore, to add an extra electron into the dot, extra energy is required to compensate the Coulomb repulsion and no current will flow until this energy is provided by increasing the voltage. This phenomenon is known as Coulomb blockade [109, 110].

3.3 Double quantum dots

After studying the composition of a single quantum dot and the electron transport through it, the next logical step is to consider systems with two or more dots. Systems with two quantum dots are known as double quantum dots (DQDs) and, since a quantum dot is regarded as an artificial atom, sometimes the DQDs are called artificial molecules. Coherent manipulation of a single surplus electron in a DQD was reported in a series of papers by Hayashi and collaborators [23, 111]. The study of the DQD is particularly interesting, as it can be regarded as a qubit taking either the degree of freedom of spin or charge of the electrons in the quantum dots, which brings obvious applications in quantum information technology [112].

Consider the following setup used by Fujisawa *et al.* in Ref. [23]. The DQD was fabricated in a GaAs/AlGaAs heterostructure with a 2DEG (figure 3.5 illustrates a scanning electron
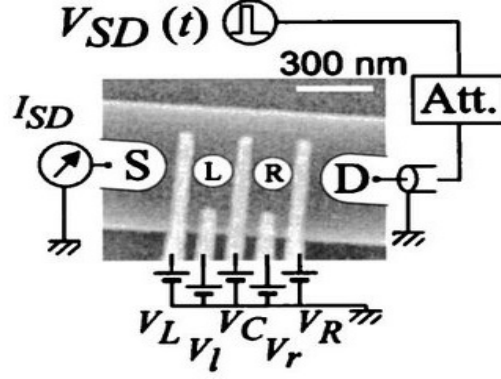
Figure 3.5 Scanning electronic transport image of the sample used by Fujisawa *et al* [23].
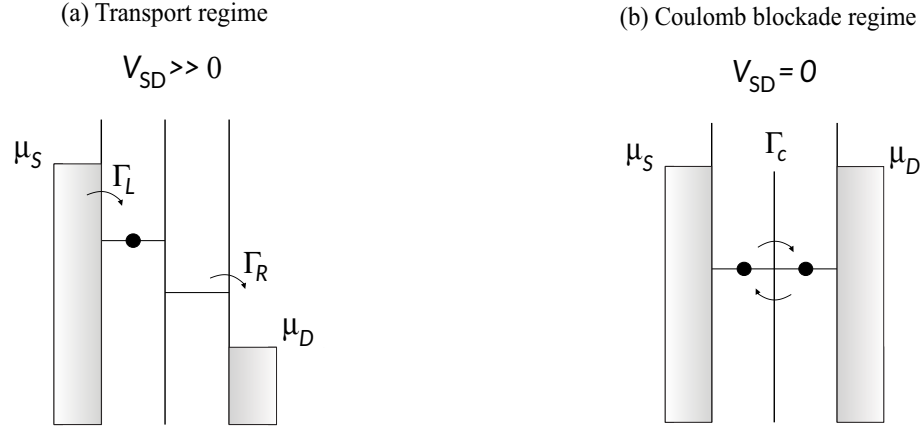

Figure 3.6 Representation of the energy diagram for the DQD in: (a) the transport regime and (b) the Coulomb blockade regime. The black ball represents the excess electron in the quantum dot.

micrograph of the DQD). The left and right dot are coupled through an interdot tunneling barrier with negative gate voltage V_C. Metal electrodes also form tunneling barriers between the source (S) and the left dot (L), and between the drain (D) and the right dot (R), both with negative gate voltages V_L and V_R, respectively. The gates with voltages V_l and V_r can also be adjusted to control the confinement potential in each quantum dot and, in general, are not the same ($V_l \neq V_r$). The main control feature is the voltage difference between the source and the drain, V_{SD}, in which the qubit state can be initialized, manipulated, and measured.
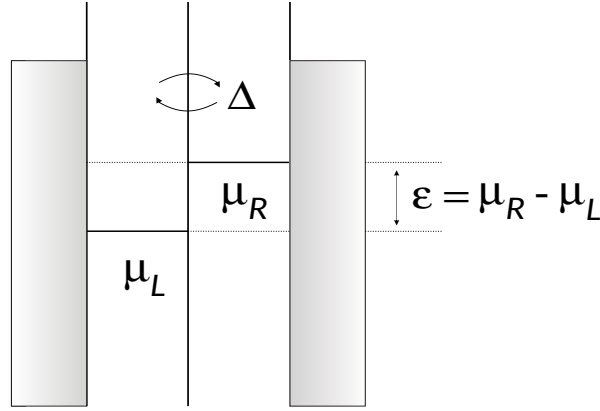
Figure 3.7 Dessintony between electronic levels of the dots, where μ_L and μ_R are the chemical potentials of the left and right dots, respectively.

Let Γ_L and Γ_R be the tunneling rate through the left and right barrier, respectively. An excess electron occupying the left dot (right dot) characterizes the state $|L\rangle$ ($|R\rangle$), $|0\rangle$ is the empty state and $|2\rangle$ is the doubly occupied state. There are two different regimes of operation for the DQD, the transport regime and the Coulomb blockade regime (see figure 3.6). The transport regime is characterized by a large source-drain voltage $V_{SD} \gg 0$, in which the continuous flow of electrons through the quantum dots implies the qubit state to be in a statistical mixture of $|L\rangle$, $|R\rangle$, $|0\rangle$ and $|2\rangle$. On the other hand, the Coulomb blockade regime is characterized by a null source-drain voltage $V_{SD} = 0$. In this regime, there is no enough energy for the electrons to surpass the Coulomb repulsion and thus there is no current flow through the DQD. During this regime, we have an artificial two-level system that defines the charge qubit, this way the qubit state can be either in $|L\rangle$ or $|R\rangle$, i.e. the excess electron is tunneling all the time from the left to the right dot and vice-versa so that we never know where the electron is. In both regimes, the system is initially prepared in the localized state $|L\rangle$ by choosing Γ_L, $\Gamma_R \gg \Gamma_c$, with Γ_c being the tunneling coupling between the left and right dots.

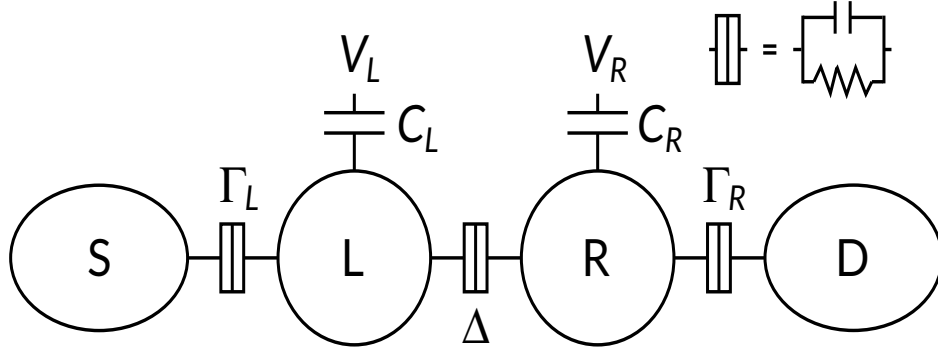In the Coulomb blockade regime, the effective Hamiltonian of the system can be described

Figure 3.8 Equivalent single-electron circuit diagram for the DQD. The tunneling barriers are characterized by a tunnel resistor and a capacitor, as indicated in the figure. This figure was adapted from Ref. [113].

as

$$\hat{H} = \frac{\varepsilon(t)}{2}\hat{\sigma}_z + \frac{\Delta}{2}\hat{\sigma}_x, \tag{3.1}$$

where σ_i $(i = x, y, z)$ are the Pauli matrices. The parameter $\varepsilon = \mu_R - \mu_L$ is the chemical potential difference of the left and right dot, which describes a possible emergence of current between the dots depending on the sign of $\varepsilon(t)$. The parameter Δ describes the strength of the tunneling coupling between the pair of quantum dots[2]. Therefore the two terms in the Hamiltonian reflect the electron oscillation in both dots by taking into account the chemical potential difference (which, in general, generates an electric current) and the quantum tunneling effect. An equivalent circuit diagram for the DQD is illustrated in figure 3.8, where the dots L and R are connected to each other by a tunneling barrier (with coupling energy Δ) and to the electrodes by tunneling barriers (with tunneling rates Γ_L and Γ_R). Each dot is also capacitively coupled to a gate voltage V_L (V_R) through a capacitor C_L (C_R).

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[2]In case you are wondering why we defined the parameter Δ since we have already previously defined the parameter Γ_c, the reason is simply that we need to redefine a new parameter that counts for the tunneling coupling exactly as Γ_c, but with dimension of energy to put the Hamiltonian in terms of it.

Chapter Four

Coupled double quantum dots heat machines

In this chapter, we provide a model for a quantum heat engine using two coupled double quantum dots (DQDs), each DQD with an excess electron to interact, as the working medium. We describe the physical model and how the quantum Otto cycle can be implemented. We also analyze the arising of different regimes of operations of our thermal machine and we show how the effects due to the quantum tunneling of a single electron between each individual DQD affects the operation modes of the engine. This model was a proposal of the research group and brings original results that are organized in an article accepted for publication in the journal Physical Review E.

4.1   The model

We proposed the following quantum system as a working medium for a quantum heat engine. Consider a two-qubit device constituted by a pair of coupled double quantum dots (DQDs) fabricated in a standard AlGaAs/GaAs heterostructure with two-dimensional electron gas (2DEG). The qubit takes the charge degree of freedom of an excess electron in each DQD, where the coupling emerges from the Coulomb interaction.
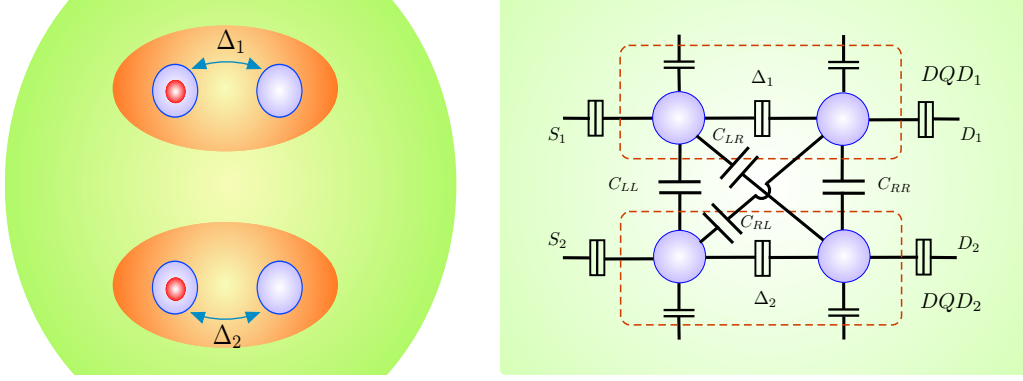
Figure 4.1 The left picture shows a schematic representation of the physical model with two coupled DQDs. The purple spheres represent the quantum dots, the electrons are represented by the smaller red spheres inside the quantum dots and $\Delta_{1,2}$ stands for the tunneling coupling of the $DQD_{1,2}$. The right picture is the equivalent circuit diagram of the device. Tunnel couplings are represented by two bars as in Δ_1 and Δ_2, $S_{1,2}$ and $D_{1,2}$ are, respectively, the source and drain of the $DQD_{1,2}$, and the capacitors C_{LL}, C_{RR}, C_{LR} and C_{RL} connect the DQDs.

The device consists of a series of tunneling barriers between the dots (characterized by the coupling energies Δ_1 and Δ_2) as well as capacitively coupled to gate voltages. The electron configurations in both DQDs are controlled by tuning the voltages applied on the gates (see Figure 4.1). On the other hand, the two double quantum dots are capacitively coupled, this capacitance model describing the Coulomb interactions between the two DQDs [25, 27, 114]. This capacitance coupling is controlled by the capacitors C_{LL}, C_{RR}, C_{LR} and C_{RL}, where no transition for the electron to leave the DQD_1 into DQD_2 is allowed, and vice-versa. The tunnel junctions placed after the source $S_{1,2}$ and before the drain $D_{1,2}$ are adjusted in such a way to make the system in the Coulomb blockade regime, enabling a single electron to be confined in each DQD. The charge of the excess electron in each DQD build up the qubits, which are described by the two possible states for the location of each electron, the left dot ($|L\rangle$) and the right dot ($|R\rangle$), where the electron can tunnel from left to right and from right to left. The Hamiltonian of such a system is given by

$$\hat{H} = \Delta_1 \hat{\sigma}_1^x + \Delta_2 \hat{\sigma}_2^x + V(\hat{\sigma}_1^z \otimes \hat{\sigma}_2^z), \tag{4.1}$$

where Δ_1 and Δ_2 are the strength of the tunneling coupling between each pair of quantum

dots, V is the interaction Coulomb coupling between the excess electrons and $\sigma_{1(2)}^{x,y,z}$ are the Pauli matrices. The tunneling coupling parameters Δ_1 and Δ_2 are controlled by the gate voltages and the electrostatic coupling V between the double quantum dots is controlled by the gates voltage sources S_1 (S_2) through the capacitors connecting both DQDs. A more general version of the Hamiltonian of this system takes into account an extra term for the energy differences between the uncoupled charged states $|L\rangle$ and $|R\rangle$ (exactly as in equation 3.1), but there is no analytical solution for this general case. This way, we consider the simplest case where all of our quantum dots have the same energy available for the electron to occupy and we can get analytical solutions.

Solving the eigenvalue equations for the Hamiltonian (4.1), we obtain the following eigenstates (see Ref. [115])

$$|\psi_1\rangle = \alpha_-[A_-(-|LL\rangle + |RR\rangle) + n_-(|LR\rangle - |RL\rangle)], \tag{4.2}$$

$$|\psi_2\rangle = \alpha_-[n_-(-|LL\rangle + |RR\rangle) + A_-(-|LR\rangle + |RL\rangle)], \tag{4.3}$$

$$|\psi_3\rangle = \alpha_+[A_+(|LL\rangle + |RR\rangle) + n_+(|LR\rangle + |RL\rangle)], \tag{4.4}$$

$$|\psi_4\rangle = \alpha_+[n_+(|LL\rangle + |RR\rangle) - A_+(|LR\rangle + |RL\rangle)], \tag{4.5}$$

where $\alpha_\pm = \frac{1}{\sqrt{2}\sqrt{(n_\pm)^2 + A_\pm^2}}$, $A_\pm = V + \sqrt{(n_\pm)^2 + V^2}$ and $n_\pm = \Delta_1 \pm \Delta_2$, with the following eigenenergies

$$E_1 = -\sqrt{(n_-)^2 + V^2}, \tag{4.6}$$

$$E_2 = -\sqrt{(n_+)^2 + V^2}, \tag{4.7}$$

$$E_3 = \sqrt{(n_-)^2 + V^2}, \tag{4.8}$$

$$E_4 = \sqrt{(n_+)^2 + V^2}. \tag{4.9}$$

An important result that we will later need is how the eigenenergies change as either the Coulomb coupling or one of the tunneling parameters increases (it does not matter which of them we take since the Hamiltonian is symmetric as we change $\Delta_1 \leftrightarrow \Delta_2$). From the

figure 4.2 we see that the energy levels are compressed pairwise and, at the same time, the ground and the first excited state are separated from the second and third excited state as the interaction coupling is raised. On the other hand, the energy levels are pairwise detached. As we increase the tunneling parameter, they are shifted apart from each other more rapidly than the energy levels separation observed inside each pair separately. Thus the energy scale variation is not uniform.
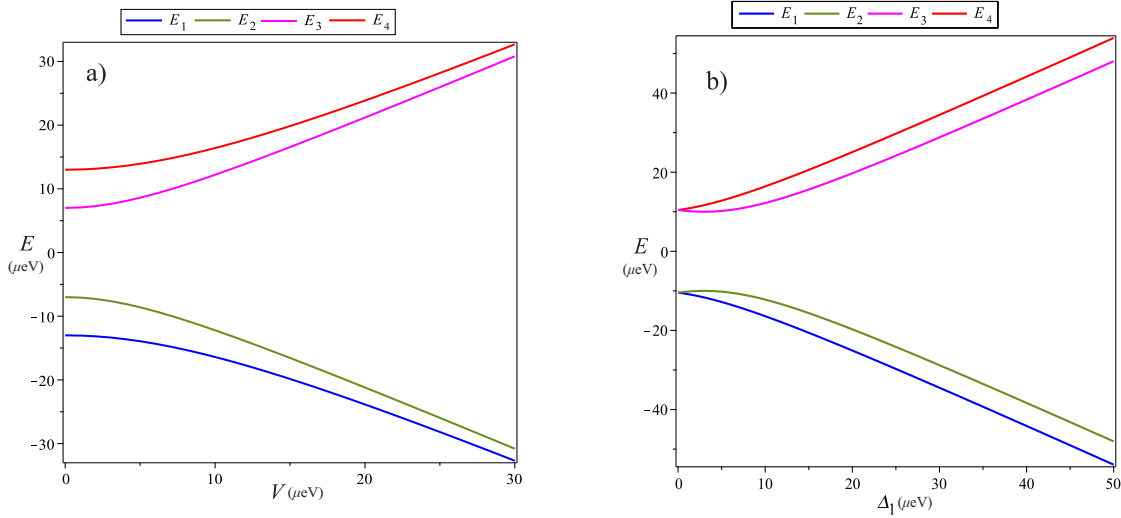

Figure 4.2 In a), it is depicted the energy levels in terms of the interaction coupling V between the two DQDs for the same fixed tunneling parameters $\Delta_1 = 10\mu\text{eV}$ and $\Delta_2 = 3\mu\text{eV}$. In b), we have the plot of the energy levels against the tunneling parameter Δ_1 for fixed $\Delta_2 = 3\mu\text{eV}$ and $V = 10\mu\text{eV}$. Notice that there is a squeezing of the energy gaps as we either increase the interaction coupling or decrease the tunneling parameter.

Despite the values of the tunneling parameters, Δ_1 and Δ_2, are mostly predetermined in the fabrication of the device, we still can modify them considerably experimentally [25].

Here we refer to the system as in a Gibbs state when it is in thermal equilibrium with a heat bath, which means that its density matrix is given by $\rho(T) = \frac{exp(-\beta H)}{Z}$, where Z is the partition function, $\beta = \frac{1}{kT}$, k is the Boltzmann constant and T is the temperature of the heat bath. In the figure 4.3 we see the occupation probabilities distribution $p_n = exp(-E_n/kT)/Z$ for the four possible states $|\psi_n\rangle_{n=1..4}$ in terms of the temperature. We see that for $T = 1\mu\text{eV}$ or even $T = 2\mu\text{eV}$ (we normalize the Boltzmann constant $k = 1$ in this whole chapter), the

second and the third excited states has practically zero probability ($p_3 \approx p_4 \approx 0$) for the system to be found in, this way we can neglect this two most excited states and approximate our system by a two-level one in this regime. On the other hand, if we have, e.g., $T = 10\mu\text{eV}$ or $T = 20\mu\text{eV}$, we see that p_3 and p_4 are no longer negligible, thus the two-level approximation is no longer valid in this regime.
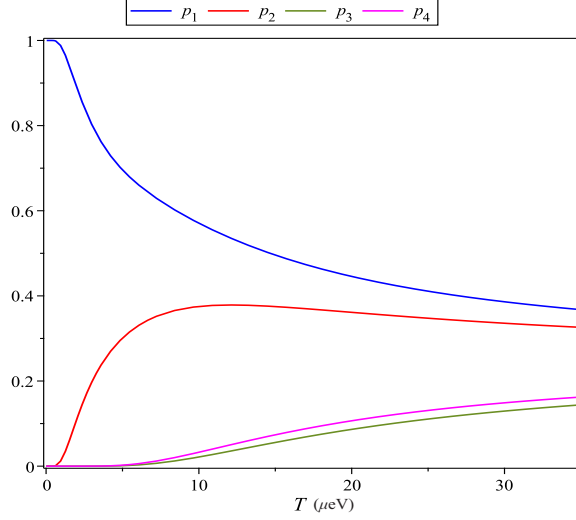

Figure 4.3 The occupation probabilities p_n against the temperature T for fixed values: $V = 10\mu\text{eV}$, $\Delta_1 = 10\mu\text{eV}$ and $\Delta_2 = 3\mu\text{eV}$.

4.2   Quantum Otto cycle

Established the physical implementations of our working medium, we now need to describe the operation of the machine. We assume a quasistatic unitary dynamics (described in chapter two, more specifically in the subsection 2.2.1), and we take the case of a quantum Otto engine, which is described by four strokes: two quantum isochoric processes and two quantum adiabatic processes (see figure 4.4).

The cycle starts with a quantum isochoric process ($A \to B$): the working medium, with interaction coupling V_h and tunneling parameters Δ_1^h and Δ_2^h, is put in contact with the hot reservoir at temperature T_h until they reach a thermal equilibrium and a total heat $Q_h > 0$
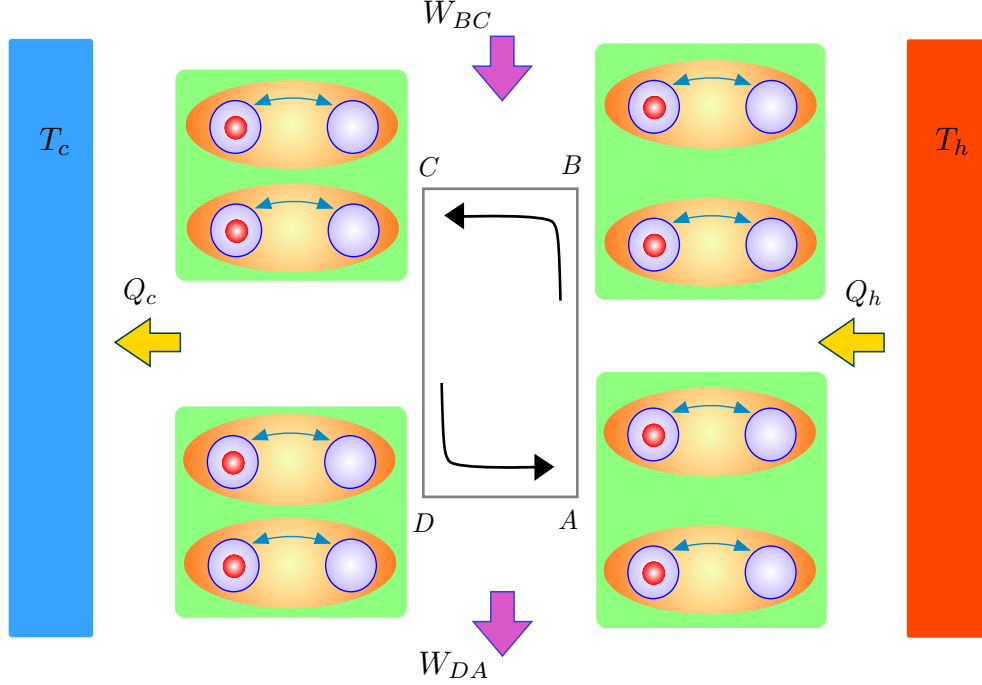
Figure 4.4 A schematic representation of an Otto engine using a pair of coupled DQDs as a working medium: the incoming heat from the hot bath, Q_h, is transformed into extracted work. The engine cycle consists of two adiabatic strokes ($B \to C$ and $D \to A$) where it is decoupled from the thermal baths, and two isochoric strokes ($A \to B$ and $C \to D$) where the engine is coupled to two thermal baths at temperatures T_h and T_c, with $T_h > T_c$.

is transferred to the system at the end of the process. The parameters V, Δ_1 and Δ_2 that regulate the eigenenergies are controlled externally, what makes this process easier to realize in an experiment. At the end of the process we will have, for the energy eigenstate basis $\{|\psi_n\rangle\}$, the following density matrix

$$\rho_h = exp(-H_h/kT_h)/Z_h = \sum_n p_n^h |\psi_n\rangle \langle\psi_n|, \tag{4.10}$$

with

$$H_h = \sum_n E_n^h |\psi_n\rangle \langle\psi_n|, \tag{4.11}$$

$$p_n^h = exp(-E_n^h/kT_h)/Z_h, \tag{4.12}$$

$$Z_h = \sum_n exp(-E_n^h/kT_h), \tag{4.13}$$

where Z_h is the partition function, p_n^h is the occupation probabilities of each eigenstate and H_h is the Hamiltonian when the system is in contact with the hot heat bath.

Next, we have a quantum adiabatic expansion (B→ C). In this process no heat is exchanged between the system and the environment. The working medium is isolated from the environment and therefore, the equation (4.12) is no longer valid during the process because there is no thermal equilibrium with it. Thus we can increase the interaction coupling from V_h to $V_c > V_h$ by adjusting the charge state through the gates voltage sources S_1 (S_2) in the capacitors mentioned in figure 4.1 and still keep the occupation probabilities p_n^h constant until the end of the process. Moreover, in parallel to this, the tunneling parameters may be tuned from $\Delta_1^h(\Delta_2^h)$ to $\Delta_1^c(\Delta_2^c)$ by controlling the gate voltages in each DQD. Thereby the energies increases from E_n^h to E_n^c, so the Hamiltonian will be given by $H_c = \sum_n E_n^c |\psi_n\rangle \langle\psi_n|$ and some work $W_{BC} > 0$ is extracted from the system.

In the next stroke we have another quantum isochoric process (C→ D). We put the working medium in contact with the cold reservoir at temperature T_c, waiting enough time for the thermalization to occur. A total heat $Q_c < 0$ is transferred to the cold reservoir at the end of the process and, since heat is exchanged, the occupation probabilities change from $p_n^h = exp(-E_n^h/kT_h)/Z_h$ to $p_n^c = exp(-E_n^c/kT_c)/Z_c$, with $Z_c = \sum_n exp(-E_n^c/kT_c)$. The density matrix will be given by $\rho_c = exp(-H_c/kT_c)/Z_c = \sum_n p_n^c |\psi_n\rangle \langle\psi_n|$ and we keep the energies E_n^c fixed.

Finally, we close the cycle with a quantum adiabatic compression (D→ A). At this point, we adjust the voltages in the capacitors again, causing the interaction coupling to change from V_c to V_h. Apart from that, the tunneling parameters may be tuned from $\Delta_1^c(\Delta_2^c)$ to $\Delta_1^h(\Delta_2^h)$ and, consequently, the energies from E_n^c to E_n^h. The Hamiltonian of the system in the end of the process is then $H_h = \sum_n E_n^h |\psi_n\rangle \langle\psi_n|$, the occupation probabilities p_n^c are kept unchanged and some work $W_{DA} < 0$ is done on the working medium.

The quantum version of the first law of thermodynamics for an unitary dynamics allows us to calculate the total heat exchanged during the isochoric processes (see equations 2.37

and 2.38), that is,

$$Q_h = \sum_n E_n^h (p_n^h - p_n^c), \tag{4.14}$$

and

$$Q_c = \sum_n E_n^c (p_n^c - p_n^h), \tag{4.15}$$

where $Q > 0$ ($Q < 0$) means that heat is absorbed (released) from (to) the heat reservoirs, respectively. Therefore, the total work W produced by the heat engine in the adiabatics is, by energy conservation, the excess heat

$$W = Q_h + Q_c = \sum_n (E_n^h - E_n^c)(p_n^h - p_n^c). \tag{4.16}$$

With that in hands, we can finally have the efficiency of our heat engine, which is calculated by $\eta \equiv W/Q_h$.

The description of the refrigerator cycle is analogous to the processes of the heat engine discussed early, except for the direction of operation of the cycle, which is reversed. This means that we will have a heat released $Q_c > 0$ from the cold heat bath and absorbed $Q_h < 0$ by the hot heat bath to the working medium and, consequently, it will be necessary an external work $W = Q_h + Q_c < 0$ for the cycle to operate. The coefficient of performance (COP) ε measures the efficiency of the refrigerator, which is defined as the modulus of the ratio of heat released from the cold heat bath and the total work done in the cycle, that is, $\varepsilon \equiv Q_c/W$.

With those definitions in hand, in the next section, we investigate in detail the work done, the efficiency η, and the COP ε of our machine.

4.3   Work and efficiency

To plot the next graphics, we restrict ourselves to the case where the tunneling parameters Δ_1 and Δ_2 are the same for the whole cycle and we will no longer worry about the upper index. This way we define a compression ratio r as the ratio between the maximum and

the minimum interaction coupling values in the cycle, $r = V_c/V_h$. As we have previously discussed, the Coulomb interaction is modified by the controlling voltages in the capacitors. Since a quantum dot is typically regarded as a 0-D system, for which the actual spatial dependence is not considered, the parameter r cannot be seen due to the changing of the volume of the system. The energy level spacing of the system is the quantity that is being either compressed or stretched.

4.3.1 Estimating the parameter values
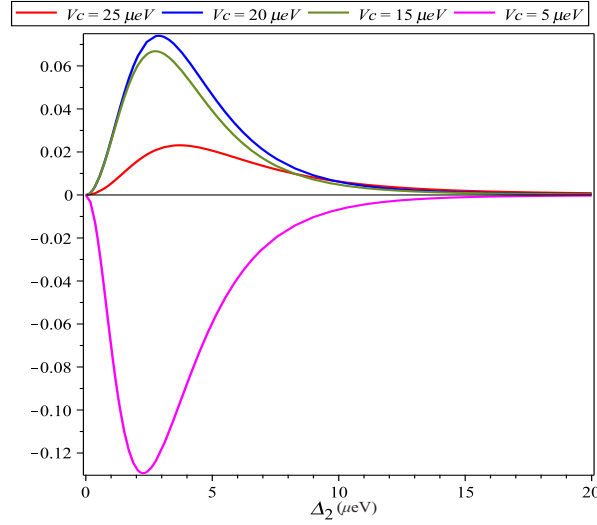
Figure 4.5 The work done against the tunneling parameter Δ_2 for different values of V_c and fixed values: $V_h = 10\mu eV$ and $\Delta_1 = 10\mu eV$. We have $V_c = 5\mu eV$ (magenta curve), $V_c = 15\mu eV$ (green curve), $V_c = 20\mu eV$ (blue curve) and $V_c = 25\mu eV$ (red curve). The case $V_c = 10\mu eV$ is not plotted, but it corresponds to a null work.

Let us settle the heat bath temperatures as $T_h = 2\mu eV$ and $T_c = 1\mu eV$ (we normalize the Boltzmann constant $k = 1$ during this whole chapter) with the purpose of approaching our system by a two-level one with eigenenergies E_1 and E_2. Fixing also $V_h = 10\mu eV$ and $\Delta_1 = 10\mu eV$ (which are common experimental values in DQDs [25–27]), the figure 4.5 shows us the work done W against the tunneling parameter Δ_2 for some different values of the Coulomb coupling V_c. Thus we can see that the peak of the curve does not shift

considerable, so we can approximately estimate the best value for Δ_2[1], at least by order of magnitude, that optimize the work done, to know $\Delta_2 \approx 3\mu eV$.

4.3.2 Engine operation modes

Now that we established the values for the parameters, we can finally obtain the plot for the work done and the efficiency of the heat engine. In the figure 4.6 the heat exchanged Q_h (Q_c) with the hot (cold) reservoir, the work done W, the efficiency η and the Carnot efficiency η_c are given in terms of the compression ratio r. It is clear from the figure 4.6 that we need $r > 1$ ($V_c > V_h$) to achieve positive work, which is reasonable because in this regime the energy gaps are squeezed (see figure 4.2) when the system is in contact with the cold reservoir and they are expanded when the system is in contact with the hot reservoir [5]. Note that we can not increase the compression ratio r indefinitely since the positive work condition is lost. As we increase the value of r, it comes to a point where there is no heat transfer even when the system is in contact with the hot and the cold reservoir. Furthermore, after this point, the signs of the heat exchanged are inverted and the system starts to withdraw heat from the cold reservoir and transfer heat into the hot reservoir. In other words, the system starts behaving as a refrigerator at cost of some work.

To summarize, we see the appearance of three different regions of operation for the heat engine. In region I the engine requires a negative work $W < 0$ to extract heat from the hot to the cold reservoir, i.e, the machine operates as a heater. In region II we have a positive work, $W > 0$, which means that it acts as a heat engine producing useful work. Finally, region III corresponds to a refrigerator as we have already discussed early, because we have an inversion in the heat flow at cost of some work $W < 0$. These results show that we can pass through the different regimes by simply increasing a single parameter, the interaction coupling V_c (which causes the change in r).

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[1]It does not matter which of the Δ's we fix, the Hamiltonian is symmetric under the change $\Delta_1 \leftrightarrow \Delta_2$ (see equation 4.1).
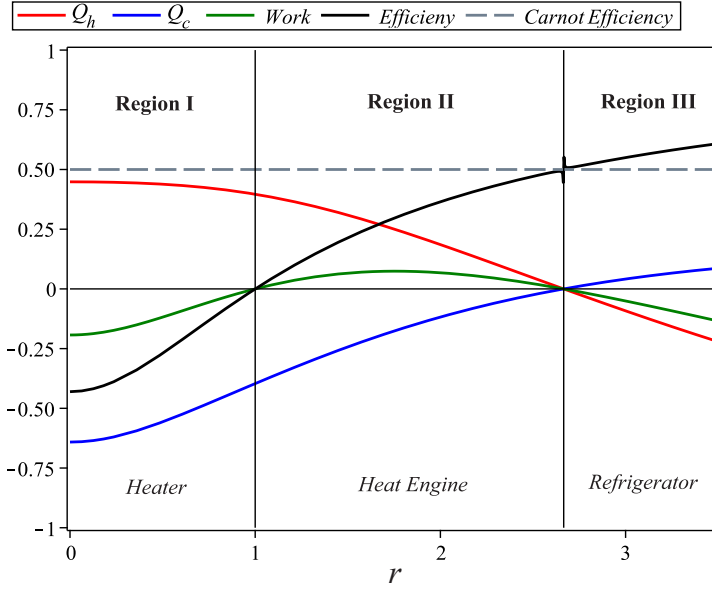
Figure 4.6 As illustrated, we have the heat exchanges of the working medium with the hot and cold reservoirs (Q_h and Q_c, respectively), the work W done, the efficiency η and the Carnot efficiency η_C of the heat engine against the compression ratio r. Heat transfer between the hot and cold reservoir. A sign inversion on the flow of the heat happens as we increase the compression ratio r. For this plot, we have chosen the values $V_h = 10\mu eV, \Delta_1 = 10\mu eV, \Delta_2 = 3\mu eV, T_h = 2\mu eV, T_c = 1\mu eV$. The values of Q_h, Q_c and W are given in units of μeV.

Notice that the two points where the green curve of the work done intersects the r-axis in the figure 4.6 have different meanings: the first one has to do with the equality in modulus of the heat Q_h and Q_c (see equation 4.16), i.e, all of the heat absorbed from the hot reservoir is released to the cold reservoir, and the second one has to do with the total interruption of the heat transferred to both reservoirs. This interruption can be explained through the occupation probabilities $p_n^h = exp(-E_n^h/kT_h)/Z_h$ and $p_n^c = exp(-E_n^c/kT_c)/Z_c$, where we can see in the figure 4.7 that there is a point where the occupation probabilities curves for the hot and cold heat baths intersects, which means that in this regime there is no change on the occupation probabilities of the system when it passes from the hot heat bath to the cold heat bath, what causes the interruption of the heat flux.

After zooming the figure 4.6, we can extract additional information about the "*point*" that causes the divergence on the efficiency plot. First of all, as we can see from the figure 4.8,
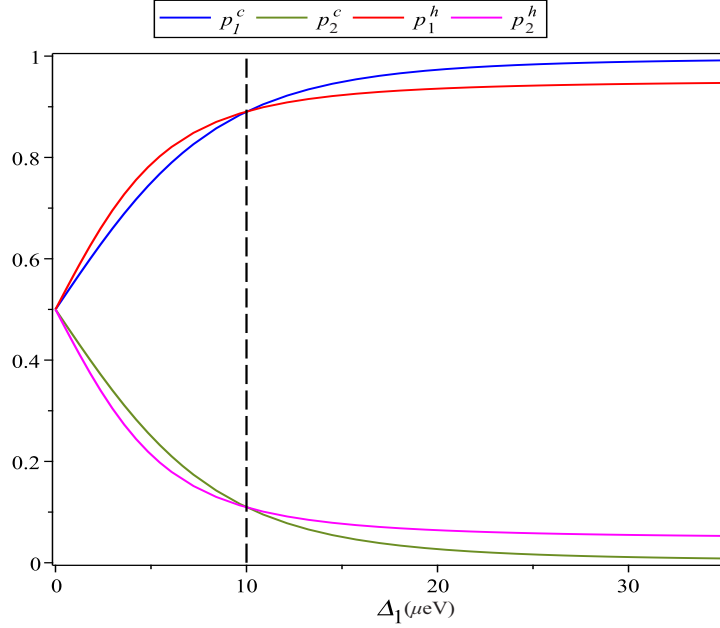
Figure 4.7 The occupation probabilities curves for the ground and first excited state in the two situations are shown, when the system is in contact with the hot heat bath and the cold heat bath. The probabilities curves for higher excited states are omitted because their values are close to zero for this values that we take, to know, $V_h = 10\mu\text{eV}, \Delta_2 = 3\mu\text{eV}, T_h = 2\mu\text{eV}, T_c = 1\mu\text{eV}$ and $r = 2.67$, which is approximately the value of the compression ratio where the inversion of the heat fluxes occurs in figure 4.6.

there is no such a thing as a point that simultaneously inverts the signs of the heat exchanged Q_h and Q_c. Before the efficiency explodes, the work tends to zero, and so the efficiency, where over again we have the heat pump regime. After an almost infinitesimal increase on r, there is an explosive increase in efficiency to infinity due to the total interruption of the heat flow Q_h (remember that $\eta = W/Q_h$). After this point, the system does not immediately starts behaving as a refrigerator, we have a tiny region where the machine consumes work and exhaust heat for both reservoirs (we use here the notations of the Ref. [116] for the two different kinds of heat pump, to know, *heater I* for the usual heater and *heater II* for the machine that heats both reservoirs, see also Ref. [117]). Only after that, we will have a positive heat flow from the cold reservoir to the system turning the machine into a refrigerator.
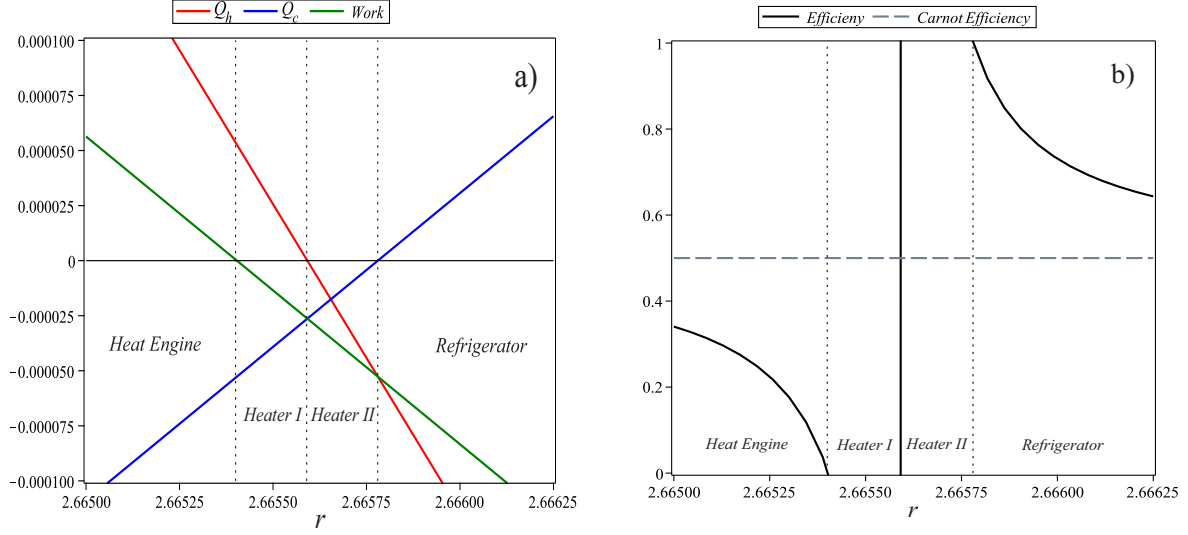
Figure 4.8 In (a) we have the work done W (green), the heat absorbed Q_h (red) and released Q_c (blue) against the compression ratio r: the observed behaviour remind us something like a phase transition. In (b), the efficiency η (solid curve) and the Carnot efficiency η_c (dashed horizontal curve) against the compression ratio r are depicted: it is observed a drastic fall intersecting the r-axis and continuing to negative values till Q_h goes to zero, where the efficiency explodes to infinity. We keep the same values, as usual, $V_h = 10, \Delta_1 = 10, \Delta_2 = 3, kT_h = 2, kT_c = 1$. The values of Q_h, Q_c and W are given in units of μeV.

4.3.3 The refrigerator regime
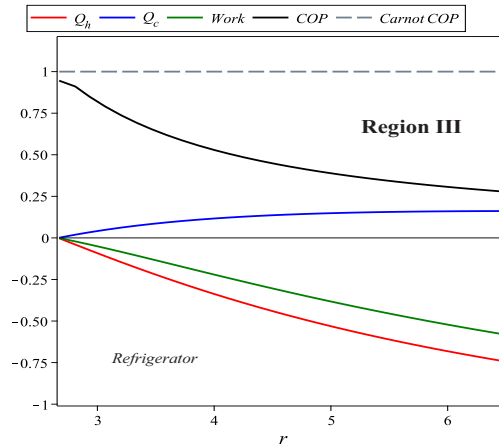
Figure 4.9 As illustrated, we have the heat exchanges of the working medium with the hot and cold reservoirs (Q_h and Q_c, respectively), the work done and the COP ε of the refrigerator against the compression ratio r. To plot this graph we have chosen the values $V_h = 10\mu$eV, $\Delta_1 = 10\mu$eV, $\Delta_2 = 3\mu$eV, $T_h = 2\mu$eV, $T_c = 1\mu$eV. The values of Q_h, Q_c and W are given in units of μeV.

After the point where the heat fluxes are inverted that we discussed previously, the machine starts behaving as a refrigerator, thus we can evaluate the COP for it. Similarly, as before, we make plots containing all the important information about the refrigerator at this stage. This is carried out in figure 4.9 where we put the heat transferred to the hot and the cold reservoirs, the work done, the COP of a Carnot refrigerator, and the COP against the compression ratio r. It is important to mention that the definition of COP is only valid in region III (see figure 4.8). Note that the COP is a monotonically decreasing function of the compression ratio.

4.3.4 The influence of the quantum tunneling

Early we have restricted ourselves to the case where there is no change on the tunneling parameters Δ_1 and Δ_2. Although we have found some interesting features for the heat engine, still nothing too different from the classical one was observed. As it is well known, quantum tunneling is not predicted by the laws of classical mechanics: for a particle to surpass a potential barrier it is required potential energy. In the light of recent papers, in particular, the Klimovsky work [118], we can extract some unexpected features of our machine if we consider the quantum tunneling. For instance, we observe a regime where work can be extracted for unchanged Coulomb coupling, which we considered to define the compression ratio. This can be achieved by varying some gate voltages that control the tunneling parameters of the DQDs.

The classical Otto engine assumes the efficiency $\eta_O = 1 - \frac{1}{r^{\gamma-1}}$, $\gamma = C_p/C_v$ being the specific heat ratio and r the compression ratio. Note that for $r = 1$ the efficiency goes to zero and if $r < 1$ the efficiency becomes negative corresponding to the heater regime. This is exactly what happens if we keep $\Delta_1^c = \Delta_1^h$ and $\Delta_2^c = \Delta_2^h$, which is depicted in the blue curves of figure 4.10, thereat we will refer this particular case as the *classical case*. At this point we can abandon the constraint we made before and consider $\Delta_1^h \neq \Delta_1^c$ and $\Delta_2^h \neq \Delta_2^c$,

so that new parameters $\delta_1 = \Delta_1^c/\Delta_1^h$ and $\delta_2 = \Delta_2^c/\Delta_2^h$ can be defined. The full description of the operation modes of the engine is no longer described by a single compression ratio r, but by the set of parameters $\{r, \delta_1, \delta_2\}$. Figures 4.10.(a) and 4.10.(c) shows us a plot for the efficiency normalized to the Carnot efficiency $\eta_N = \eta/\eta_c$ in terms of r for some different values of the quantities δ_1 and δ_2, and figures 4.10.(b) and 4.10.(d) shows us a plot for the coefficient of performance normalized to the Carnot COP $\varepsilon_N = \varepsilon/\varepsilon_C$, with ε_C being the Carnot COP, for the same set of parameters values used in (a) and (c), respectively.

Let us take a deeper look in figure 4.10.(a). In the red curve, which corresponds to the case where $\delta_1 = 1$ and $\delta_2 < 1$, it is observed an enhancement in the efficiency for lower values of r in comparison to the classical case. As a consequence, no heat pump regime appears, which means that the heater was changed to a highly efficient engine and we now have a positive efficiency even for unchanged Coulomb coupling, for which $r \equiv 1$. Also, the point of inversion from heat engine to refrigerator is shifted to a lower value of r. On the other hand, when $\delta_{1(2)} > 1$ (green curve), we have a larger region for the operation of the heat pump, and the point of inversion from heat engine to refrigerator is also shifted, but to a higher value of r instead. This means that the efficiency is reduced for lower values of r in comparison to the classical case, but part of the region that previously described the refrigerator is now valid for a highly efficient engine.

In the figure 4.10.(c), the magenta curve, which corresponds to the case where $\delta_1 > 1$ and $\delta_2 < 1$, is a stretching of the blue curve. There is an expansion of the operation of the heat engine in both directions, taking the old heater regime and also part of the old refrigerator regime. On the other hand, the orange curve, which corresponds to the case where $\delta_1 < 1$ and $\delta_2 > 1$, is a squeezing of the blue curve. All of the regime of operation for the heat engine is compressed in a shorter interval of the compression ratio r in comparison to the classical case.

The figures 4.10.(b) and 4.10.(d) illustrate the normalized COP of the refrigerator complementing the normalized efficiency plots. When the efficiency function finds a maximum,
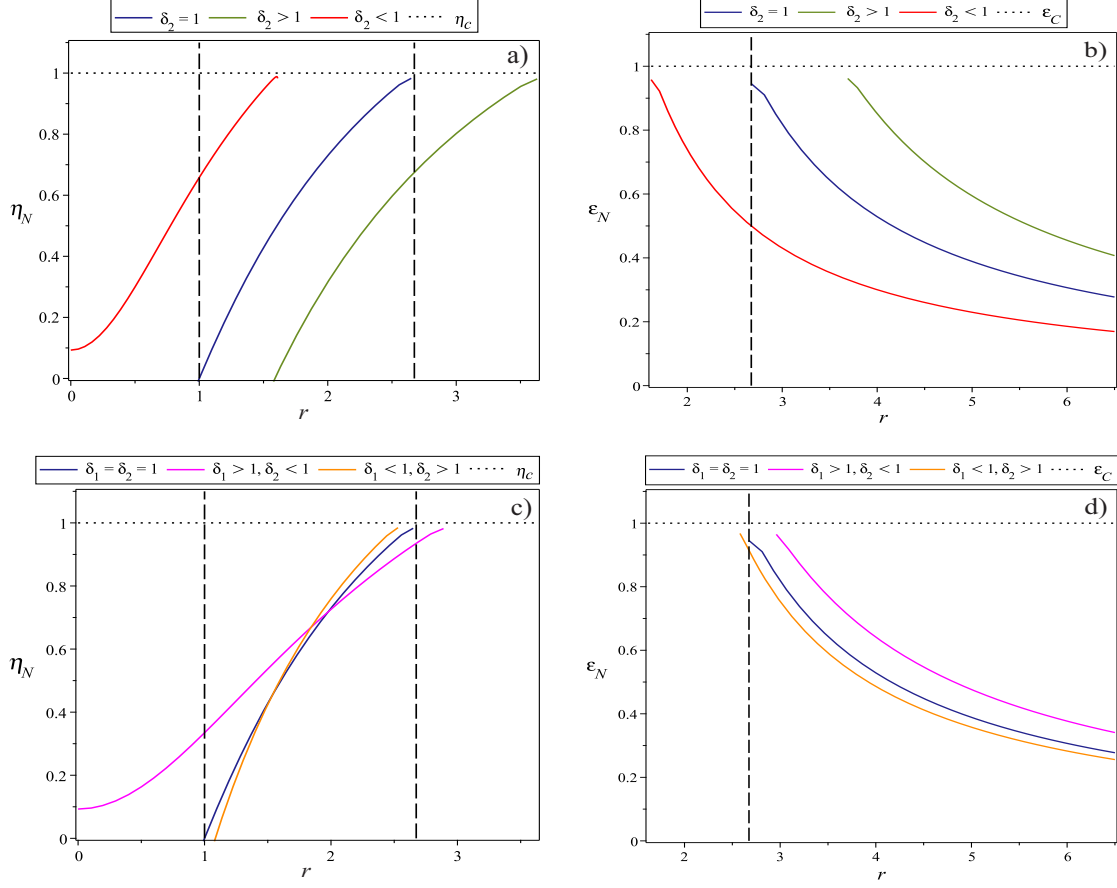
Figure 4.10 In (a), it is depicted the normalized efficiency η_N and in (b), it is shown the normalized COP ε_N curve. It is considered in both of them $\delta_1 = 1$: the classical case ($\delta_2 = 1$, blue), the $\delta_2 > 1$ case (with $\Delta_2^c = 4\mu$eV, green) and the $\delta_2 < 1$ case (with $\Delta_2^c = 2\mu$eV, red). In (c) and in (d), we have the normalized efficiency η_N and the normalized COP ε_N, respectively: the classical case ($\delta_1 = \delta_2 = 1$) in blue, the stretched magenta curve for $\delta_1 > 1$ and $\delta_2 < 1$ (with $\Delta_1^c = 18\mu$eV and $\Delta_2^c = 2\mu$eV) and the squeezed orange curve for $\delta_1 < 1$ and $\delta_2 > 1$ (with $\Delta_1^c = 7\mu$eV and $\Delta_2^c = 4\mu$eV). For all the plots we have set $V_h = 10\mu$eV, $\Delta_1^h = 10\mu$eV, $\Delta_2^h = 3\mu$eV, $T_h = 2\mu$eV, $T_c = 1\mu$eV. We observe a shift of the curve to the left (right) in comparison to the classical case when we have $\delta_{1(2)} < 1$ ($\delta_{1(2)} > 1$) individually or we can have a stretching (squeezing) for the left and right if we have $\delta_1 > 1$ and $\delta_2 < 1$ ($\delta_1 < 1$ and $\delta_2 > 1$) simultaneously, where $\delta_{1(2)}$ stands for "δ_1 or δ_2".

the inversion of the heat fluxes occurs and the engine starts behaving as a refrigerator. The colors used are the same as in (a) and (c) since the set of parameter values used are also the same.

In short, we have shown that a quantum Otto engine with two coupled DQDs as a working

medium may show different performances by tuning the tunneling parameters Δ_1 and Δ_2 withal the Coulomb potential. We have observed the possibility of work extraction even for the case where the Coulomb coupling is kept constant. Moreover, we have observed the change in the operation mode of the machine as well.

4.3.5   Beyond two-level approach

If we increase the temperatures of the reservoirs, the most excited states in the system become more relevant. For the following plots, we fix the temperatures of the reservoirs as $T_h = 20\mu eV$, $T_c = 10\mu eV$ (figure 4.3 confirms that this is enough to leave the two-level approach). In this limit, there is no sign inversion for the fluxes of heat exchanged with the reservoirs as we can see in figure 4.11.(a). The machine will never turn into a refrigerator, which sustains our explanation from the figure 4.7 where the inversion of the flow of the heat occurs because of the inversion on the occupation probabilities. Figure 4.11.(b) shows that the machine presents unusual properties even without varying the tunneling parameters, although no work can be done for $r \equiv 1$. In the region $r < 1$, the machine behaves as a heat engine producing useful work, and for $r > 1$ the machine will be a heat pump.
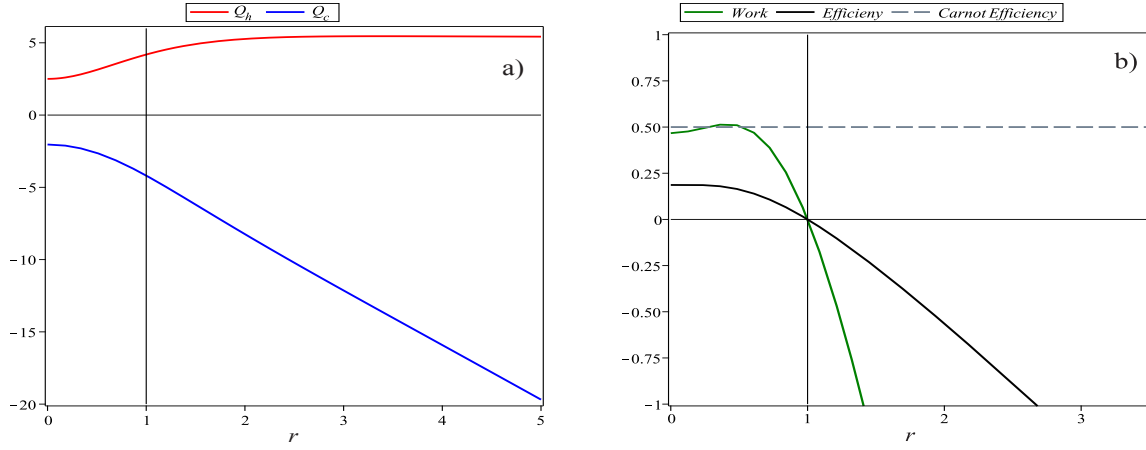
Figure 4.11 In (a) we have the heat exchanged with the hot (red curve) and cold (blue curve) reservoirs and in (b) it is depicted the work done (green curve) and the efficiency (black curve) against the compression ratio r. We have fixed $V_h = 10\mu\text{eV}, \Delta_1^h = 10\mu\text{eV}, \Delta_2^h = 3\mu\text{eV}, T_h = 20\mu\text{eV}, T_c = 10\mu\text{eV}$. The values of Q_h, Q_c and W are given in units of μeV.

Chapter Five

Conclusions

This research aimed to address a theoretical proposal for a quantum heat machine with two coupled double quantum dots interacting via Coulomb interaction of excess electrons inside each double quantum dot, which in turn acts as our charged qubits. By analyzing the corresponding quantum Otto cycle in the equilibrium regime, we have shown the appearance of different regions of operation for our machine: the heat pump, the heat engine, and the refrigerator. These operation modes can be switched by adjusting the value of the interaction coupling. We also discussed why these transitions occur and what is truly happening with the machine in the null work points. We have observed that the performance of both the engine and the refrigerator can be modified due to the manipulation of the parameters that account for the quantum tunneling of the electrons in the double quantum dots. The experimental description of our model is minutely described from the construction of the quantum dots with the heterostructures to the experimental parameters used in the engine.

This dissertation intended to be self-sufficient with the addition of a broader review on thermodynamics and statistical mechanics at an undergraduate level, but there are also engaging discussions about more recent developments in the field generally absent in the undergraduate textbooks.

The foundations of quantum thermodynamics are still a hot topic of debate that is constantly being refined, this way a more current review is always very welcome. This

dissertation gives a classification of the laws of quantum thermodynamics from different perspectives followed by the description of quantum thermal engines in different regimes of operation. Some of the latest results in the field were included in the review.

Although some ideal conditions were imposed on our proposed engine like the equilibrium condition during the whole cycle and no description of the couplings with the heat baths were specified, the possibility of an experimental realization of the machine is not totally out of the question since we have used a very usual experimental setup together with plausible parameters values. Thus, this research opens questions for possible future works, like how the coupling with the heat baths could affect the engine and how time can play a role in the thermodynamic processes.

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