T.R.
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IRREVERSIBLE QUANTUM THERMODYNAMIC PROCESSES AND QUANTUM HEAT ENGINES

MASTER OF SCİENCE

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MUSTAFA ÇANDIR

ABSTRACT

IRREVERSIBLE QUANTUM THERMODYNAMIC PROCESSES AND QUANTUM HEAT ENGINES
MSC THESIS
MUSTAFA ÇANDIR
BOLU ABANT IZZET BAYSAL UNIVERSITY
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This thesis is devoted to quantum thermodynamics where I examine the extension of the laws, processes, and cycles of thermodynamics to quantum mechanical systems. I show that, for example, the zeroth law of thermodynamics cannot be directly extended to the quantum domain due to the lack of a temperature operator. Specifically, the Carnot and Otto cycles are extended for a general quantum system. The implications of quantum mechanics on the construction of a reversible Carnot cycle are revealed. Full quantum mechanical cycle description and the quantum formulation of the second law are given for the irreversible Carnot cycle.

KEYWORDS: Classical Thermodynamics. Quantum Thermodynamics. Otto Cycle. Carnot Cycle**.** Irreversible Process.

ÖZET

TERSİNMEZ KUANTUM TERMODİNAMİKSEL SÜREÇLER VE KUANTUM ISI MAKİNALARI
YÜKSEK LİSANS TEZİ
MUSTAFA ÇANDIR
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Bu tez, termodinamiğin yasalarının, süreçlerinin ve döngülerinin kuantum mekanik sistemlere uzantısını incelediğim kuantum termodinamiğine ayrılmıştır. Örneğin, termodinamiğin sıfır yasasının, bir sıcaklık operatörünün olmaması nedeniyle doğrudan kuantum alanına genişletilemeyeceğini gösteriyorum. Spesifik olarak, Carnot ve Otto döngüleri genel bir kuantum sistemi için genişletilir. Kuantum mekaniğinin tersine çevrilebilir bir Carnot döngüsünün inşası üzerindeki etkileri ortaya çıkarılmıştır. Tam kuantum mekanik döngü tanımı ve ikinci yasanın kuantum formülasyonu, geri dönüşü olmayan Carnot döngüsü için verilmiştir.

ANAHTAR KELİMELER: Klasik Termodinamik. Kuantum Termodinamiği. Otto Döngüsü. Karnot Döngüsü. Geri Dönüşü Olmayan Süreç.

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LIST OF ABBREVIATIONS AND SYMBOLS

$\mathbf{Q}$	**:** Heat
$\mathbf{U}$	**:** Internal Energy
$\mathbf{W}$	**:** Work
$\boldsymbol{\eta_c}$	**:** Classical Carnot efficiency
$\boldsymbol{\eta}$	**:** Efficiency
$\mathbf{T_H}$	**:** Hot Heat Reservoir Temperature
$\mathbf{T_L}$	**:** Cold Heat Reservoir Temperature
$\mathbf{Q_H}$	**:** Hot Heat Reservoir
$\mathbf{Q_L}$	**:** Cold Heat Reservoir
$\mathbf{E_n}$	**:** Energy Levels
$\boldsymbol{\rho}$	**:** Density Operator
$\boldsymbol{\mathcal{L}}$	**:** Efficiency Lag
$\boldsymbol{\lambda}$	**:** Tuning Parameter
$\mathbf{S}$	**:** Entropy

1. INTRODUCTION

In the last few decades, there have been a constantly increasing interest in thermodynamic of systems at the quantum level[1-66]. In this research field, the following fundamental questions arise: how do the four fundamental laws of thermodynamics emerge at the quantum level? How can the work and heat be defined for quantum mechanical systems? How are the fundamental laws and the thermodynamic processes affected by the quantum features, such as the discreteness of states, quantum coherence and entanglement? Along this line, integrating and adapting thermal machine cycles and classical thermodynamic processes to the quantum regime have been an active research field of study[1,3]. 3-level maser was introduced a long time ago as a kind of quantum heat engine that can produce useful work at the classical Carnot efficiency [4]. Since then, numerous cautionary suggestions[5,12] and empirical realizations[13,18] of the nanoscale thermal machines have been carried out.

A quantum heat engine is simply defined as the machine operating through a thermodynamic cycle which uses the quantum systems as the working medium and/or the heat bath. Both thermal and quantum fluctuations impress the operation of such engines. The main objective in such studies is to utilize the role of the quantum sources such as quantum coherence, entanglement and quantum interaction as a benefit in the work extraction[19,29]. Numerous latest studies have demonstrated that a heat engine with quantum resources can be more efficient than the Carnot cycle[19,24].

Carnot cycle is one of the cornerstones of classical thermodynamics which is an ideal cycle comprised of two adiabatic and two isothermal processes. It is reversible when all strokes are quasistatic. The efficiency of the Carnot cycle is the upper bound for all other thermodynamical cycles which is determined only by the ratio of the two heat bath temperatures involved in the thermodynamic process, namely $\eta_c = 1 - T_L/T_H$. Here T_H (T_L) denotes the hot (cold) heat bath temperature. The type of the working substance has no importance on this efficiency. Exceeding η_c is regarded as the violation of the second law of thermodynamics.

A number of studies have been recently devoted to the quantum construction of the Carnot cycle[1,33,46,50,53]. In the quantum regime, beside the quasi-static condition, the reversibility of the Carnot cycle requires the working medium to be scale-invariant[1]. We mean for the "scale-invariant" condition here that all the energy levels should be altered by the same ratio in the two quantum adiabatic processes. If the isothermal steps of the cycle are quasistatic, the quantum working medium is always in thermal equilibrium at the reservoir temperature. However, the scale invariance property is the condition that makes the working medium to be in a canonical distribution undergoing a quasistatic adiabatic process. If one can properly adjust the scaling quantity, the working substance would define an effective temperature which can be equal to the heat bath temperature. Under the above aforementioned requirements, there would be no irreversible entropy production. Then, the quantum Carnot cycle is thermodynamically reversible which operates at the classical Carnot efficiency, i.e., $\eta_c = 1 - T_L/T_H$[1].

Due to the scaling requirement, it is not an easy task to construct a thermodynamically reversible Carnot cycle for quantum systems[47,48]. For quantum mechanical systems such as a qubit, a simple harmonic oscillator, and uncoupled arbitrary spins, the scaling requirement is inherently established[1,61]. However, when a coupled quantum system or anisotropic cases are considered, it would not be an easy process to justify the scaling requirement. Recent studies employed the two Heisenberg XXX and anisotropic XY coupled spins 1/2 as the working medium of the reversible quantum Carnot cycle which showed that the frequency and the interaction strength are required to be simultaneously altered during all the strokes of the cycle in the same ratio[34,62]. Experimentally, it can be easier to alter and control one of the external quantities in the coupled quantum working medium. In such a case, the working substance may not fulfill the scale invariance requirement. Therefore, the dynamical evolution during the quantum adiabatic process may not keep the Boltzmann thermal distribution even it is quasistatic. When the working medium gets in contact with the reservoir before the isothermal stroke, a thermalization process is inevitable which makes the quantum cycle irreversible.

In this thesis, the main objective is twofold. On one hand, to keep the thesis self-consistent, we review the known thermodynamics ideas, laws, processes, and Otto and Carnot cycle for both classical and quantum cases. Those results are presented in sections 2 and 3. On the other hand, in section 4 we give a microscopic state description of the Carnot cycle for quantum systems that have non-scalable energy levels[70]. Similar formalisms for the quantum Carnot cycle have also been given in Reference[46,47]. The main difference in the construction of the cycle as discussed in Reference[46,47] arises from the irreversible thermalization processes [see also Reference[69] for the comparison of two approaches]. In Reference[46] the thermalization processes are considered as the stages that conserve the total mean energy of the working substance. In this approach, only the entropy increases while the working medium thermalizes. The main obstacle in the approach is the requirement of careful control and choice of the external parameters in the quantum adiabatic stage to keep the internal energy invariant in the subsequent thermalization process. On the other hand, the approach given in Reference[47] is more simple which considers the thermalization processes simply the quantum version of the classical isochoric processes. The external parameters are kept unchanged during the thermalization. Heat is exchanged, therefore the mean energy of the working substance changes. The parameters are free to choose in the quantum adiabatic stages. In this thesis, we use the scheme given in Reference[48] and consider the thermalization processes as the quantum version of the classical isochoric stages. In Reference[48], it is shown that the Carnot cycle efficiency is directly connected to the total entropy increase of the universe which is interpreted to be smaller than the classical Carnot efficiency due to the irreversibility. We have extended the results in Reference[47] and given full microscopic interpretation of the Carnot cycle[70]. The total entropy increase of the universe is connected to the relative entropy which is shown to justify the second law of thermodynamics. The ideas and the developed theory for the Carnot cycle is examined for an example where two Heisenberg coupled spins are considered as the working medium.

2. THERMODYNAMICS AND HEAT ENGINES FOR CLASSICAL SYSTEMS

This thesis aims to investigate the quantum mechanical version of the Carnot cycle for two-coupled spins 1/2 systems as the working medium. Before doing this investigation and making this thesis self-consistent, we start with the investigation of the classical thermodynamic laws, classical thermodynamic processes, and the Carnot cycle for the ideal gas[65]. After the discussion of classical concepts, we extend the laws of thermodynamics, the thermal processes, and the Carnot cycle to the quantum domain.

2.1 Temperature and the Zeroth Law of Thermodynamics

We first define an important quantity for classical systems called temperature. The temperature for classical systems (i.e., macroscopic objects) is a well-defined quantity. It can be measured, for example, by touching a celsius thermometer to a body and waiting for the thermometer to approach a static value. For example, we accept the room temperature of approximately 25°C. After defining the temperature, we can discuss the zeroth law of classical thermodynamics. This law defines thermal equilibrium. Let us state law with an example. Let say we have three objects, A, B, and C. If objects A and object B are separately in thermal equilibrium with object C, we can then easily state that the objects A and B are in thermal equilibrium. How can an observer be sure that the objects are all in thermal equilibrium? The answer is of course by using a thermometer. If the observer measures the temperatures of the object A, B, and C, he/she will get the same value. So one can think that the temperature is a quantity that determines whether or not the two objects are in thermal equilibrium.

We discuss the quantity temperature and the zeroth law for classical systems in depth. Because the extension of temperature and thermal equilibrium for quantum systems are not so simple as a classical one. We will see in the following discussion that temperature and thermal equilibrium can be defined under certain conditions for quantum systems.

2.2 The First Law of Thermodynamics

The first law of thermodynamics is just the law that states the conservation of energy in any thermodynamic process. Before starting the law, we should express and understand some concepts and definitions in thermodynamics, such as internal energy, heat and work.

We first define the internal energy of a system. The internal energy is defined as the total energy of the system contributed from its microscopic components. For example, for a system composed of molecules, the internal energy is the sum of all energy including the translation kinetic energy, vibration and rotation energy of the molecules, and the potential energy between the molecules. We use the symbol U to indicate the internal energy.

As a second concept, we define heat. In thermodynamics, heat is defined as a kind of energy that is exchanged across the boundaries of the system when it is in contact with another body having a different temperature. In this thesis, we use the symbol Q for heat.

As the last concept, we define the work done by the system. To understand this more clearly, let us consider an ideal gas confined in a tube with a movable piston. Let say the walls of the tube is isolated from the surrounding, then the heat exchange is zero. The change of the volume of the tube is regarded as the gas doing work on the outside. The work done by the gas denoted by the symbol W written as

$$\mathrm{W}= \int_{Vi}^{Vf} PdV \tag{1}$$

where Vi (Vf) is the initial (final) value of the volume and P represents the pressure of the gas.

Now we define the first law of thermodynamics which states that the change in the internal energy ΔU can be done by adding heat to the system and/or doing work by the system. Mathematically, it can be formulated as

$$\Delta \mathrm{U}=\mathrm{Q}\text{-}\mathrm{W} \tag{2}$$

We would like to mention the sign convention for the heat and work that will be used throughout the thesis. The positive (negative) Q indicates the heat

absorbed (rejected) by the system, while positive (negative) W indicates the work done by on the system.

2.3 Thermodynamic Processes

Heat engines, refrigerators, and heat pumps are generally composed of four thermodynamic processes which are adiabatic, isochoric, isothermal, and isobaric processes. For example, the automobile's gasoline engine is just an Otto cycle that is composed of two isochoric and two adiabatic processes. Another example is Diesel engines which are comprised of two adiabatic processes, one isochoric and isobaric process. Therefore, it is important to understand the basic mechanisms of the thermodynamic processes.

We first define the adiabatic process. In an adiabatic process, there is no heat exchanged of the system with its surrounding. Therefore, the heat $Q=0$. According to the first law of thermodynamics, the change in internal energy can be done by only work in an adiabatic process i.e.,

$$\Delta U=-W. \tag{3}$$

In an isochoric process, no work is done since it occurs at a constant volume. Therefore, the change in the internal energy can be done by only heat exchange in an isochoric process.

In an isothermal process, the system is coupled to a huge body which is called a heat bath. Having a high degree of heat capacity so that its temperature never changes during the process. Heat can be exchanged with the heat bath and work can be done by the system. For the isothermal process, the changes should be done very slowly to keep the system temperature invariant. In short, an isothermal process is one that happens at an invariant temperature.

In an isobaric process, the pressure should be constant. Similar to the isothermal process, the system is coupled to the heat bath. However, different from the isothermal process, the temperature is not constant. For example, remember the equation of the state of an ideal gas which is $PV=nRT$. For an expanding gas, to keep the pressure constant, the temperature should be increased

properly. This process should be quasi-static. Both work and heat are non-zero during the process.

2.4 The Second Law, Entropy, and the Classical Heat Engines

This thesis aims to give a microscopic state description of the Otto and Carnot heat cycles for general quantum systems. Before doing this, we analyze the classical mechanical version of the Otto and Carnot heat engine cycles. A heat engine, which operates in a cycle, converts some fraction of gained heat energy to useful work. A simple representation of a heat engine is given in figure (1).

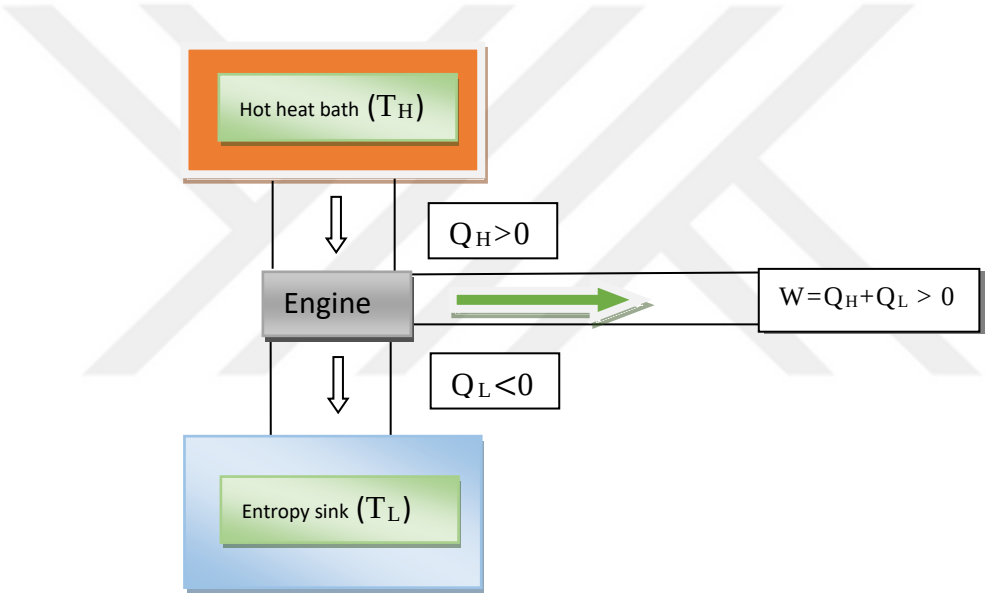

Figure 1. A simple diagram of a heat engine. $Q_H > 0$ amount of heat is absorbed from the hot heat bath at temperature T_H. $W = Q_H + Q_L > 0$ amount of work is done by the engine, while $Q_L < 0$ amount of heat is rejected to the entropy sink at temperature T_L. For a working medium of the engine, we consider an ideal gas with an equation of state $PV = nRT$, where n and R are the amount of substance and ideal gas constant, respectively.

The working medium in heat engines encounters a thermodynamic cycle, such as Carnot or Otto cycle. In a cycle, the change in internal energy is zero, i.e., $\Delta U=0$. According to the first law of thermodynamics, the net absorbed heat by the

engine from the heat baths is equal to the net work produced by the engine. If we denote Q_H and Q_L (see figure 1) as the net heat exchanges with the hot and cold heat reservoirs, respectively, the net work done by the heat engine is

$$W = Q_H + Q_L \tag{4}$$

For the heat engine operation, the sign conversion is simply given as $Q_H > -Q_L > 0$,i.e., $W > 0$. Next, we define the performance parameter of the heat engine which is measured by the thermal efficiency η. The quantity η is the measure of the ratio of the benefit to the input. For the heat engines, the benefit is the work done by the heat engine (W) while the input is the heat absorbed from the high-temperature heat bath (Q_H). Accordingly;

$$\eta = \frac{W}{Q_H} = 1 + \frac{Q_L}{Q_H}. \tag{5}$$

Now we define the second law of thermodynamics and state its implication for the heat engine. The second law of thermodynamics describes the processes which can occur spontaneously. For example, heat flows from the hot body to the cold body, which is a spontaneous process. Such a process does not violate the second law. However, a process that heat flows from a colder body to a hotter body with no external forces cannot occur spontaneously and violates the second law of thermodynamics. For the heat engines, the second law of thermodynamics, states that there is no heat engine with 100% efficiency. In other words, for a cyclic heat engine, the work output can never be equal to Q_H. That is some heat must be given to the entropy sink. Therefore, the second law states that the heat engine efficiency should be smaller than 100%. This statement is known as the Kelvin-Planck statement of the second law for heat engines. When we analyze the Carnot cycle, a more strict restriction for the heat engine efficiency will be given.

2.5 The Carnot Heat Engine Cycle

In 1824, a researcher named Sadi Carnot proposed a theoretical heat engine cycle that has great importance for classical thermodynamics. The cycle is named by his name, i.e., the Carnot cycle[62]. The Carnot heat cycle is comprised of four ideal, reversible processes, namely two reversible isothermal and two

reversible adiabatic processes. The Carnot cycle is powerless since it processes quasistatically. However, it is the most efficient heat engine among all other thermodynamic heat engine cycles. If we denote the hot and cold heat reservoir temperatures, respectively as T_H and T_L, the Carnot efficiency is given as $\eta_c = 1 - T_L/T_H$. According to Carnot's theorem, which is one of the formulations of the second law of thermodynamics for heat engines, no thermodynamic heat engine cycle efficiency can be greater than η_c. In other words, η_c is the upper limit for the heat engine cycle.

Let us consider a Carnot heat engine cycle for an ideal gas as the working medium. The processes are depicted in figure (2), where we plot the pressure (P) versus volume (V) of the ideal gas. Let us examine the processes in detail.

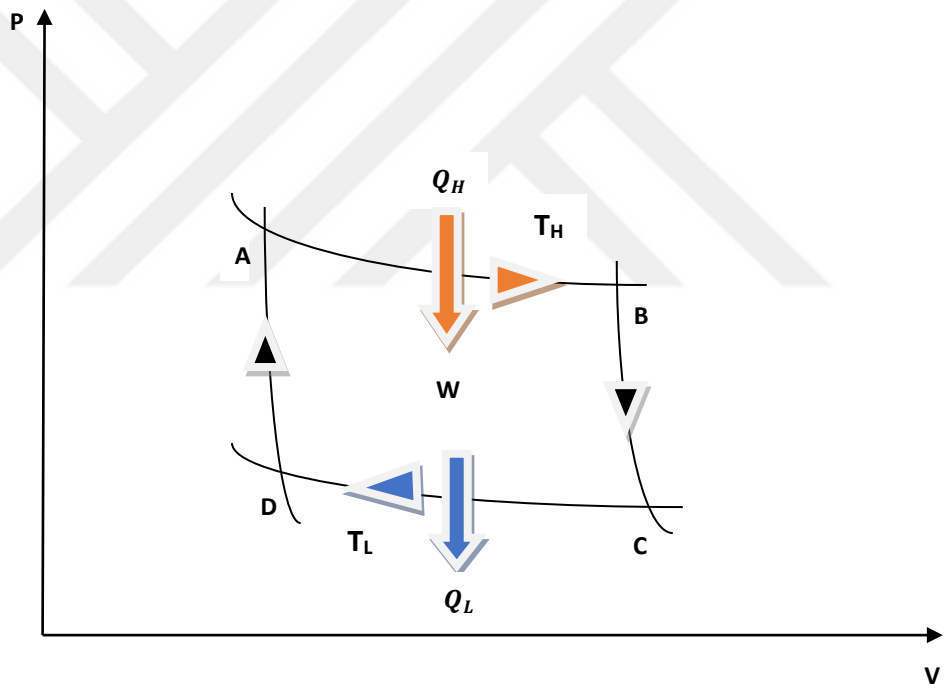

Figure 2. Pressure (P) versus volume (V) diagram of the classical Carnot heat engine cycle for an ideal gas as the working medium. Please recall that the area inside the closed PV diagram gives work (W) done by the ideal gas.

A → B: The process is a quasistatic isothermal process. The working medium is coupled to the hot heat bath and is always at thermal equilibrium at the reservoir temperature T_H. For an ideal gas, the change in internal energy is zero for an

isothermal process. Therefore the absorbed heat Q_H from the hot heat bath is all converted to the work, i.e., $W_{AB} = Q_H$ where W_{AB} denoted the work done by the ideal gas in the process from A to B. Then the heat absorbed can be calculated as

$$Q_H = W_{AB} = \int_A^B PdV \tag{6}$$

$$= nRT_H \ln(V_B/V_A) > 0 \tag{7}$$

B → C: The process is a quasi-static adiabatic process. There is no heat bath, so no heat is exchanged. Only work is done by the ideal gas. For the adiabatic processes of the ideal gas, the multiplication $TV^{\gamma-1}$ is all the same at every instant (where γ is the adiabatic exponent which is constant). Then, we can write for the process B → C,

$$T_H V_B^{\gamma-1} = T_L V_C^{\gamma-1} \tag{8}$$

C → D: This is another isothermal process where the working medium is at thermal equilibrium at temperature T_L. The rejected heat can be calculated similarly

$$Q_L = W_{CD} = \int_C^D PdV \tag{9}$$

$$= nRT_L \ln(V_D/V_C) < 0 \tag{10}$$

D → A : This is another adiabatic process. For the beginning and end of the process, it can be written as

$$T_L V_D^{\gamma-1} = T_H V_A^{\gamma-1} \tag{11}$$

Now we are ready to calculate the Carnot efficiency,

$$\eta_c = 1 + \frac{Q_L}{Q_H} \tag{12}$$

$$= 1 + (nRTL \ln(V_D/V_C))/(nRTH \ln(V_B/V_A)) \tag{13}$$

$$= 1 - \frac{T_L}{T_H} \tag{14}$$

In the above calculation, we used the relations in equation (8) and equation (11) which gives that $T_H/T_L = (V_D/V_A)^{\gamma-1} = (V_C/V_B)^{\gamma-1}$. Therefore $\ln(V_D/V_C) = -\ln(V_B/V_A)$. Consequently, η_c in the equation (13) reduces to $\eta_c = 1 - T_L/T_H$. Please remark here that while analyzing the Carnot cycle, we implicitly stated that the ideal gas is in thermal equilibrium at the reservoir temperatures at the end of the adiabatic processes. This is justified by equations (8) and (11) which guarantees the thermal equilibrium states at temperatures T_L and T_H at instants C and A.

2.6 The Otto Heat Engine Cycle

Otto cycle is another example of a thermodynamic cycle which is composed of two adiabatic and two constant volume (isochoric) processes[1]. The Otto cycle has found many applications in the real world, for example in automobiles as a gasoline engine. The pressure versus volume diagram for an ideal gas encountering the Otto cycle is simply schematized in figure (3). Let us discuss its strokes in detail.

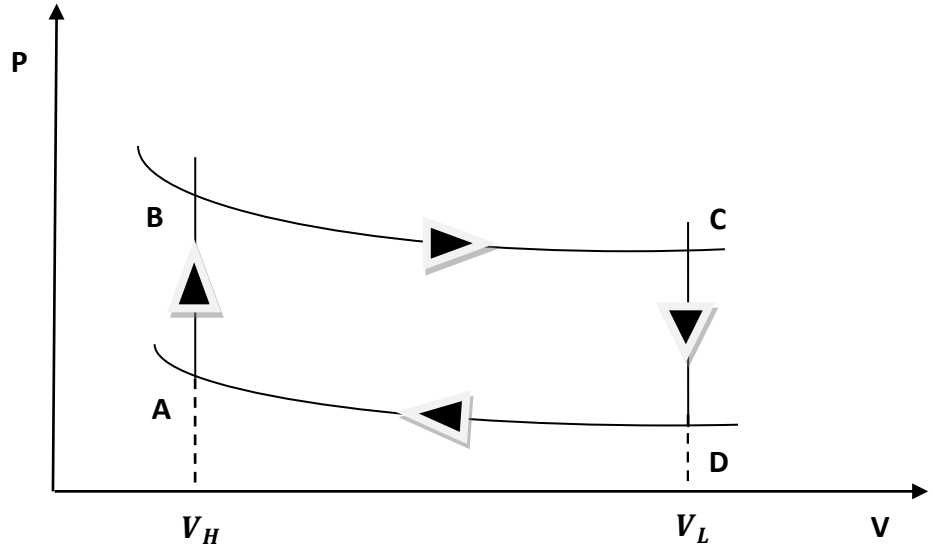

Figure 3. Pressure versus volume diagram of the classical Otto heat engine based on an ideal gas as the working medium. V_H and V_L denote the volume of the gas during the isochoric heating and cooling processes, respectively.

A → B: The first process is the classical isochoric process where the ideal gas is in contact with the hot heat bath at temperature T_H. Since the process is executed at a constant volume V_H, no work is done. At the end of the process (at instant B), the gas is thermalized at the hot reservoir temperature. An amount of heat is absorbed which can be given as

$$Q_H = \int_A^B C_V \, dT = C_V(T_H - T_A). \tag{15}$$

Here C_V denotes the heat capacity of the ideal gas at constant volume (which is $C_V = \frac{3}{2}nR$) and T_A is the temperature of the gas at instant A.

B → C: The process is the adiabatic expansion process where work is done by the gas on the outside. Please remark here that for the adiabatic evolution of an ideal gas the multiplication $TV^{\gamma-1}$ is constant. Therefore one can write

$$T_H V_H^{\gamma-1} = T_C V_L^{\gamma-1} \tag{16}$$

Here T_C denotes the temperature of the gas at instant C.

C → D: This process is the classical isochoric cooling process where the gas is thermalized at the cold reservoir temperature T_L. The amount of rejected heat can be given as

$$Q_L = \int_{T_C}^{T_L} C_V \, dT = C_V(T_L - T_C) \tag{17}$$

D → A: This process is the adiabatic compression process which is characterized by the following relation

$$T_L V_L^{\gamma-1} = T_A V_H^{\gamma-1} \tag{18}$$

In the Otto cycle, $\Delta U = 0$. Therefore, the net work done by the ideal gas is equal to $W = Q_H + Q_L$ which is also equal to the area enclosed by the curves in figure (3). The heat to work efficiency is equal to

$$\begin{aligned} \eta &= 1 + \frac{Q_L}{Q_H} \\ &= 1 + \frac{T_L - T_C}{T_H - T_A} \\ &= 1 - (V_H/V_L)^{\gamma-1} \end{aligned} \tag{19}$$

To find the last expression in equation (19), we used the relations in equations (16) and (18). Let us work on the equation more and find an alternative expression that will make sense when we discuss the Otto cycle for quantum systems having a special character on its energy spectrum. From equation (16) and (18), we can write

$$(V_H/V_L)^{\gamma-1} = \frac{T_L}{T_A} = \frac{T_C}{T_H} \tag{20}$$

Then the efficiency can be expressed as an alternative way.

$$\eta = 1 - \frac{T_L}{T_A} = 1 - \frac{T_C}{T_H} \tag{21}$$

Please remark that in the Otto cycle (figure 3), the highest temperature is T_H while the lowest one is T_L. Therefore, the efficiency of the Otto cycle given in equation (21) is always smaller than the Carnot heat engine cycle efficiency,

$$\eta_C = 1 - \frac{T_C}{T_H}. \quad (22)$$

3. THERMODYNAMICS AND HEAT ENGINES FOR QUANTUM SYSTEMS

In this section, we will develop the thermodynamic laws and processes, and construct the Otto and Carnot heat engine cycles for quantum systems with computable energy levels[1]. The Hamiltonian of the quantum system, in a general form, can be written as

$$H = \sum_n E_n \, |n><n| \quad (23)$$

where E_n are the energy eigenvalues, and $|n>$ are the corresponding energy eigenstates. To develop the theory of quantum thermodynamics, we need to define the level populations P_n which can be determined from the density operator ρ of the quantum systems, i.e., $P_n = tr(\rho|n><n|)$. An example that we will encounter in the following text, is the thermal equilibrium state. If a quantum system is in a thermal equilibrium with a heat bath, the density operator of the quantum systems can be given by the Boltzmann-Gibbs distribution, $\rho = {}^{1}/_{Z}\, e^{-\beta H}$, where $\beta = (k_B T)^{-1}$ is the inverse temperature, k_B is the Boltzmann constant, and $Z = tr(e^{-\beta H})$ is the partition (normalization) constant[66]. The level populations for the thermal state are given by the canonical ensemble $P_n = {}^{1}/_{Z}\, e^{-\beta E_n}$, which is very familiar to us in the study of statistical mechanics.

3.1 Zeroth Law of Thermodynamics for Quantum Systems

Recall that the zeroth law of classical thermodynamics defines the concepts of temperature and the thermal equilibrium for macroscopic systems (see section 2.1). However, for quantum mechanical systems, it is not always possible to define the temperature and the thermal equilibrium between quantum systems since there is no proper definition of temperature operator $\hat{T}$ in quantum mechanics. We can define the temperature for a quantum system only under some certain conditions. Let us study the concepts of temperature and the thermal

equilibrium, and the interpretation of zeroth law for the following example set up as given in Figure (4).

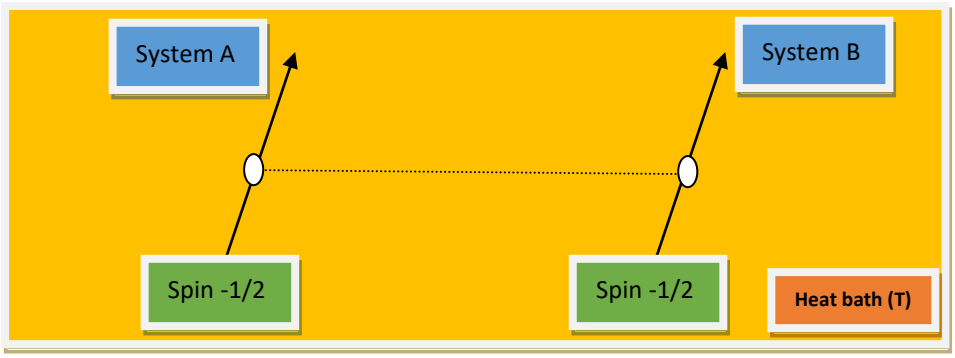

Figure 4. Two interacting spins 1/2 are embedded in a heat reservoir at temperature T. The dashed horizontal line between spins denotes the quantum interaction with strength μ.

In Figure (4), we consider two spins 1/2 which are interacting through isotropic Heisenberg XXX interaction. The corresponding Hamiltonian can be written as[67],

$$H = {}^{1}/_{2}\,\hbar\omega(\sigma_z^A + \sigma_z^B) + \mu(\sigma_x^A.\sigma_x^B + \sigma_y^A.\sigma_y^B + \sigma_z^A.\sigma_z^B), \qquad (24)$$

where $\sigma_i^{A(B)}$ $(i = x, y, z)$ are the Pauli matrices for the system A (B) in Figure (4), $\hbar = {}^{h}/_{2\pi}$ is the reduced Planck's constant, ω is the transition frequency and μ is the interaction strength.

In the standart computational basis $\{|1> \equiv |1_A 1_B>, |2> \equiv |1_A 0_B>, |3> \equiv |0_A 1_B>, |4> \equiv |0_A 0_B>$ where $|0_i>$ or $|1_i>$ denotes the spin down or up state for the i^{th} spin -1/2 },the matrix form of the Hamiltonian (24) can be written as

$$H = \begin{pmatrix} \mu+\omega & 0 & 0 & 0 \\ 0 & -\mu & 2\mu & 0 \\ 0 & 2\mu & -\mu & 0 \\ 0 & 0 & 0 & \mu-\omega \end{pmatrix}, \qquad (25)$$

The spectrum of H can be calculated as

$$E_1 = -3\mu, \qquad |E_1> = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ -1 \\ +1 \\ 0 \end{pmatrix} \qquad (26)$$

$$E_2 = \mu, \qquad |E_2> = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ -1 \\ -1 \\ 0 \end{pmatrix} \tag{27}$$

$$E_3 = \mu - \omega, \qquad |E_3> = \begin{pmatrix} 0 \\ 0 \\ 0 \\ +1 \end{pmatrix} \tag{28}$$

$$E_3 = \mu + \omega \qquad |E_4> = \begin{pmatrix} +1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \tag{29}$$

We consider here that two spins are embedded in a heat bath at temperature T. We consider the interaction between the spins with the heat reservoir is weak. Under Born-Markov approximation, the time evolution of the reduced density matrix of the two spins is in Lindblad form[66], i.e., ($\hbar = 1$)

$$\dot{\rho} = -i[H, \rho] + \mathcal{L}[\rho] \tag{30}$$

where $\mathcal{L}[\rho] = \sum_{\omega_{ij}} \Upsilon(\omega_{ij}) \left(A(\omega_{ij})\rho A^{+}(\omega_{ij}) - \{A^{+}(\omega_{ij})A(\omega_{ij}), \rho\}/2\right)$ is sumed to be performed over all energy differences $\omega_{ij} = E_i - E_j$, $\Upsilon(\omega_{ij})$ defines the emission and absorption rates, $A(\omega_{ij})$ and $A^{+}(\omega_{ij})$ are the ladder operators which obeys $[H, A(\omega_{ij})] = -\omega_{ij}A(\omega_{ij})$. We will not deal with the time-evolution. We only consider the steady state solution, i.e., the density matrix at the limit $t \to \infty$. Solving the steady state solution $\dot{\rho} = 0$ gives the Boltzmann-Gibbs distribution by all means[66].

$$\rho = {}^{1}/_{Z}\, e^{-\beta H} \tag{31}$$

$$= \sum_n P_n |n><n| \tag{32}$$

where $P_n = {}^{1}/_{Z}\, e^{-\beta E_n}$ are the Boltzmann-Gibbs occupation probabilities.

Using the spectrum in equation (26-29), the matrix form of ρ can be written as

$$\rho = \begin{pmatrix} P_4 & 0 & 0 & 0 \\ 0 & \frac{1}{2}(P_1 + P_2) & \frac{1}{2}(P_2 - P_1) & 0 \\ 0 & \frac{1}{2}(P_2 - P_1) & \frac{1}{2}(P_1 + P_2) & 0 \\ 0 & 0 & 0 & P_3 \end{pmatrix}. \quad (33)$$

To define the temperatures of the spins, we need to find its reduced density matrix. For system A, the reduced density matrix can be calculated by taking partial trace over the system B, i.e.,

$$\rho_A = \mathrm{tr}_B \rho \quad (34)$$

$$= \frac{1}{2}\begin{pmatrix} P_1 + P_2 + 2P_4 & 0 \\ 0 & P_1 + P_2 + 2P_3 \end{pmatrix}. \quad (35)$$

Similarly, the reduced density matrix for the other spin 1/2 can be given as

$$\rho_B = \mathrm{tr}_A \rho \quad (36)$$

$$= \frac{1}{2}\begin{pmatrix} P_1 + P_2 + 2P_4 & 0 \\ 0 & P_1 + P_2 + 2P_3 \end{pmatrix}. \quad (37)$$

where we find here that $\rho_A = \rho_B$.

The local Hamiltonians for the spin 1/2 can be written

$$H_A = H_B = {}^1\!/_2\, \hbar\omega\sigma_z \quad (38)$$

$$= {}^1\!/_2\, \hbar\omega \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (39)$$

Please remark here that the local density matrices A and B in equations (36) and (38) are diagonal in terms of local energy eigenvectors given in equation (41). In order to define a temperature for a quantum system, we consider that every energy levels satisfy the Boltzman distribution. Therefore by taking the following ratio for any energy levels,

$$\frac{P_n}{P_m} = \frac{e^{-E_n/(k_B T)}/Z}{e^{-E_m/(k_B T)}/Z} = e^{-(E_n - E_m)/(k_B T)} \quad (40)$$

$$k_B T = \frac{E_n - E_m}{\ln P_m - \ln P_n} \quad (41)$$

If we express our words more clearly, to assign a temperature to a quantum system we consider that (i) the density matrix is diagonal in terms of energy eigenbasis (no coherence in energy frame) and (ii) every energy levels satisfy the Boltzmann distribution, $P_n = {}^1\!/_Z\, e^{-\beta E_n}$. If (i) and/or (ii) are violated then it is not

possible to talk about the temperature for any quantum system. For a two-level system (spin 1/2) we have only one energy gap and from reduced density matrices in equations (35) and (37), the condition (i) is satisfied. Therefore, we can always define an effective temperature to the local spin -1/2 which can be calculated as

$$T_A = T_B = \frac{E_2^A - E_1^A}{\ln P_1^A - \ln P_2^A} \tag{42}$$

$$= \frac{\omega}{2\mathrm{ArcTanh}\left[\frac{-1+e^{\frac{2\omega}{T}}}{1+e^{\frac{\omega}{T}}\left(1+e^{\frac{4\mu}{T}}+e^{\frac{\omega}{T}}\right)}\right]} \tag{43}$$

where $E_n^A = E_n^B \equiv \{{}^1\!/_2\,\hbar\omega, -{}^1\!/_2\,\hbar\omega\}$ are the energy levels for system A or B and $P_n{}^A$ are the local populations given in Equation (35). We plot the local temperatures of spins 1/2 in figure (5).

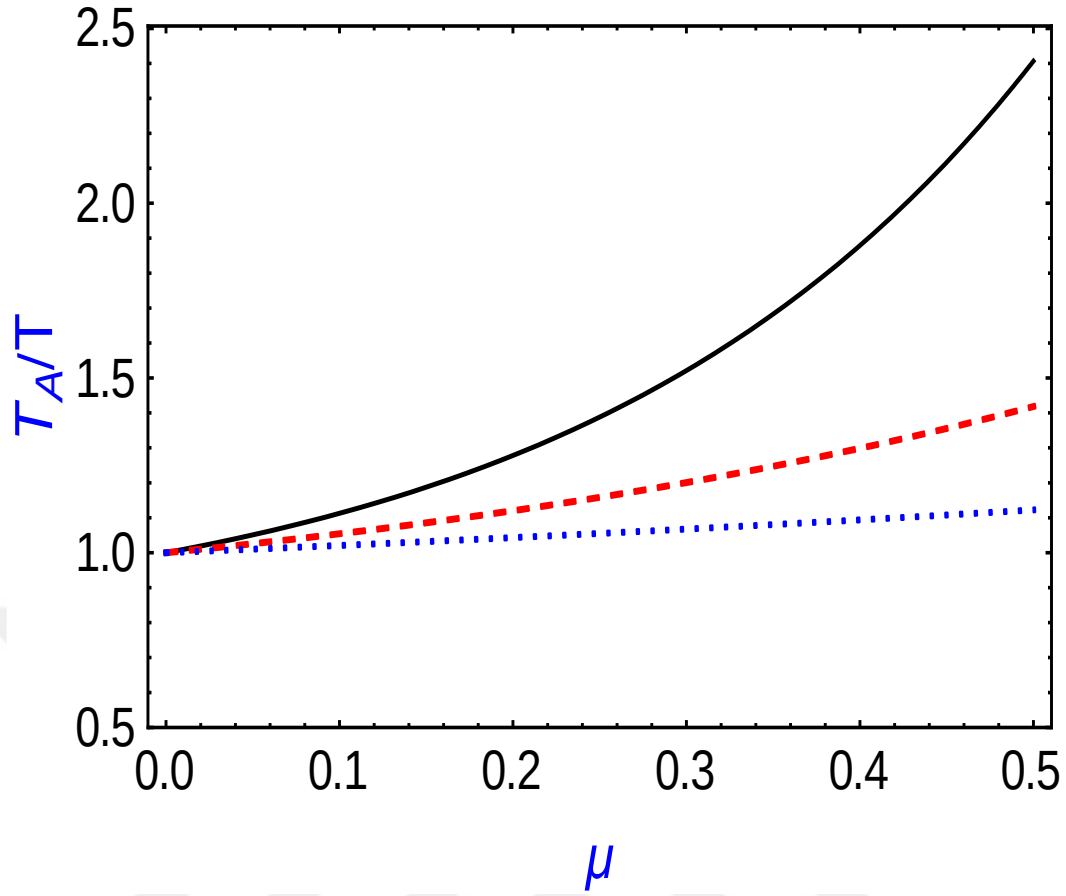

Figure 5. The local temperature T_A divided by the heat bath temperature T versus interaction strength for the values ω=1.0 and T=1.0 (black, solid line), T=2.0 (red, dashed line), and T=5.0 (blue, dotted line). We use dimensionless units where ħ= k_B= 1.

The figure demonstrates the ratio T_A/T versus interaction strength μ for the values ω =1.0 and T=1.0,2.0,5.0. The figure clearly shows the violation of the zeroth law of thermodynamics, unless μ=0. For μ>0, T_A=T_B>T. This shows that the quantum interaction between spins monotonically increases the local temperatures of the spins which is higher than the heat bath temperature T. We can claim without a doubt here that the quantum features, like entanglement, coherence, interactions, etc., can make the spins to have temperatures higher than the reservoir temperature. Even the two qubits are in thermal equilibrium with the heat bath as given by the thermal density matrix in equation (31), locally they are at different temperatures. In more complex cases, we cannot even calculate the local temperatures. For instance, if we consider even more interacting models such as Heisenberg XX, XY, and XYZ or Dzyaloshinskii-Moriya type

interactions, the local density matrices can possess coherence in the energy frame, so the definition of temperature will fail. On the other hand, for the case μ=0, the equation (43) produces $T_A = T_B = T$, since $\rho = \rho_A \otimes \rho_B$ and $\rho_i = {}^{1}/_{Z_i}\, e^{-\beta H_i}$ (i=A, B) which satisfies the zeroth law of classical thermodynamics.

3.2 The First Law of Thermodynamics for Quantum Systems

Please recall here that the Hamiltonian of the working medium is $H = \sum_n E_n |n><n|$. The internal energy is

$$U =< H >= tr(\rho H) \tag{44}$$

$$=\sum_n P_n E_n \tag{45}$$

where $P_n =< n|\rho|n >$. The infinitesimal change in the internal energy is $dU = \sum_n \{E_n dP_n + P_n dE_n\}$, which defines the first law of thermodynamics $dU = đQ + đW$ if we make the following identifications[1].

$$đQ=\sum_n E_n\, dP_n \tag{46}$$

$$đW = \sum_n P_n\, dE_n \tag{47}$$

Equations (46) and (47) suggest that work is done by/on the system only by the change of eigenenergies E_n, while the change in level populations P_n leads to the heat exchange. Please remark here that the definition $đQ=\sum_n E_n\, dP_n$ is general and universal for quantum mechanical transformations which can reduce to the classical well-known definition $đQ = TdS$ for thermal equilibrium cases if $P_n = {}^{1}/_{Z}\, e^{-\beta E_n}$ $(\beta = (k_B T)^{-1})$[1,2,69].

3.3 Thermodynamic Processes for Quantum Systems

After the definition of zeroth and first laws and also the temperature for quantum systems, we can proceed to describe the thermodynamic processes and the cycles for quantum mechanical systems. The thermodynamic processes for quantum systems and their comparison with their classical analogs are shown in table (1). The details are as follows.

	Isothermal	Isochoric	Adiabatic
Quantum	Heat exchanged Work done INV: T VAR: U, E_n, P_n	Heat exchanged No work INV: E_n VAR: T , P_n	No heat Work done INV: P_n VAR: T , E_n
Classical	Heat exchanged Work done INV: T, U VAR: P,V	Heat exchanged No work INV: V VAR: T , P	No heat Work done VAR: T , P, V

Table 1. Quantum thermodynamic processes and their comparison with the classical analogs. For the classical system, we consider an ideal gas. INV or VAR indicate invariant or variant physical quantity.

3.4 Isothermal Processes for Quantum Systems

In the quantum isothermal process, the working medium is coupled to a heat bath while its energy levels and the corresponding level populations are altered. Accordingly, both work and heat are exchanged. If the process is slow enough, the working medium is always in a thermal equilibrium state at the heat bath temperature T. The density matrix of the working medium at every instant can be written as $\rho = {}^{1}/_{Z}\, e^{-\beta H}$. Accordingly, the level populations at every time are given by the Boltzmann distribution, i.e., $P_n = {}^{1}/_{Z}\, e^{-\beta E_n}$.

3.5 Isochoric Processes for Quantum Systems

Like in the classical case, the quantum system is in contact with a heat bath during the quantum isochoric process. The system parameters (consequently,

E_n) are fixed in a quantum isochoric process, so only heat is exchanged. At the end of the process, the working medium is thermalized with the heat bath and the level populations satisfy the Boltzmann distribution, i.e., $P_n = {}^{1}/_{Z}\, e^{-\beta E_n}$.

3.6 Adiabatic Process for Quantum Systems

An adiabatic process is mainly defined as a thermodynamic process where the working medium is detached from the heat bath and its parameters are changed during the process. Since there is no reservoir, heat is not exchanged. Only work is performed due to the change in energy levels E_n. If the process proceeds quasistatically, the initial level populations P_n are maintained as given by the celebrated quantum adiabatic theorem[1]. According to Equation (47), since $dP_n = 0$ for the quantum adiabatic process, $đQ = 0$. But $đW \neq 0$, since $đE_n \neq 0$.

3.7 Quantum Carnot Cycle

Please recall here that the classical Carnot cycle, which was investigated in detail in section 2.5, provides the upper limit for the thermal efficiency, $\eta_c = 1 - T_L/T_H$ of any classical thermodynamical cycle. In the present and next sections, we will comprehensively analyze the quantum mechanical version of the Carnot cycle for an arbitrary quantum mechanical system.

The quantum Carnot cycle, like as it classical version, is comprised of two reversible quantum isothermal and adiabatic processes. The cycle diagram is simply schematized in figure (6) where we plot the internal energy $< H >$ versus the tuning parameter λ for an arbitrary working medium with discrete energy levels E_n.

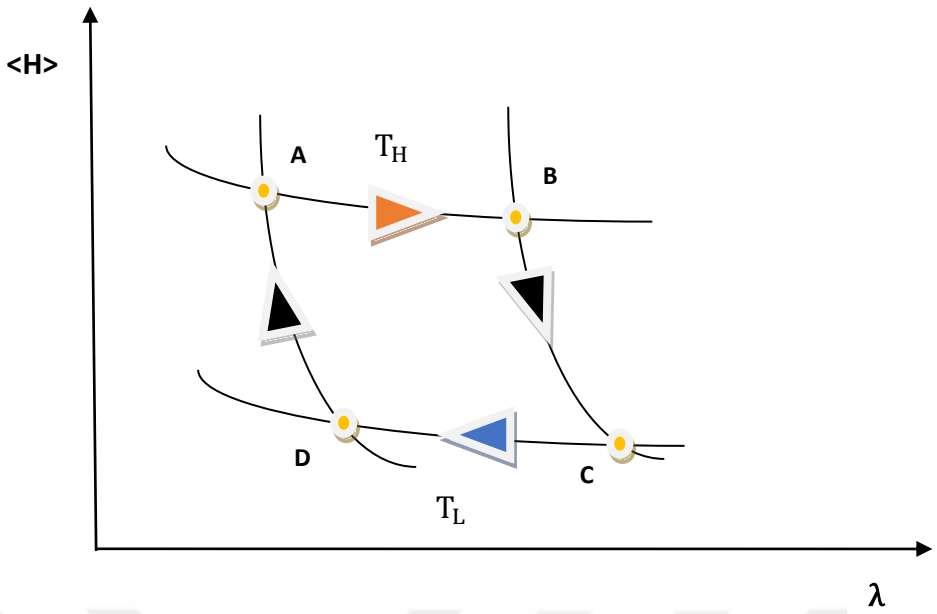

Figure 6. The cycle diagram for the reversible quantum Carnot cycle. All strokes are considered to be quasi-static. Here $< H >$ is the average (internal) energy and λ is the external control parameter that governs the cycle.

The stroke from A (C) to B (D) is the quantum isothermal process where the system keeps in thermal equilibrium with the heat bath at temperature T_H (T_L). The energy levels $E_n(\lambda)$ are tuned quasistatically via a controlled external parameter λ. The exchanged heat can be calculated through classical equation $đQ = TdS$, where $S(i) = -k_B \sum_n P_n(i) \ln P_n(i)$ is the entropy and $P_n(i) = {}^{1}/_{Z(i)}\, e^{-\beta(i)E_n(i)}$ (i=A,B,C,D) are the Gibbs probability distribution of each energy levels. The stroke from B (D) to C (A) represents quantum adiabatic process where the level populations are invariant, i.e., $P_n(B) = P_n(C)$ and $P_n(D) = P_n(A)$. To ensure the cycle reversibility, at instant C (or A), the working medium should be in thermal equilibrium at the reservoir temperature T_L (T_H). This strict condition requires all energy gaps to be changed in the same ratio during the quantum adiabatic processes[1]. Mathematically, the energy levels should be scalled in the following form

$$E_n(\lambda_A) - E_m(\lambda_A) = \frac{T_H}{T_L}[E_n(\lambda_D) - E_m(\lambda_D)] \tag{48}$$

$$E_n(\lambda_B) - E_m(\lambda_B) = \frac{T_H}{T_L}[E_n(\lambda_C) - E_m(\lambda_C)] \tag{49}$$

Let us prove that the above conditions ensure the working medium to be at an effective temperature at the reservoir temperature. Consider the adiabatic process from B to C. Let us state that at instant C, the working medium is in an effective temperature T_C^{eff}. According to the quantum adiabatic process, $P_n(C) = P_n(B) = 1/Z(B)e^{-E_n(B)/k_B T_H} = 1/Z(C)e^{-E_n(C)/k_B T_C^{eff}}$. If we take the ratio and use the above scaling assumption,

$$\frac{P_n(B)}{P_m(B)} = \frac{P_n(C)}{P_m(C)} = \frac{\frac{e^{-E_n(B)/k_B T_H}}{Z(B)}}{\frac{e^{-E_m(B)/k_B T_H}}{Z(B)}} = \frac{\frac{e^{-E_n(C)/k_B T_C^{eff}}}{Z(C)}}{\frac{e^{-E_m(C)/k_B T_C^{eff}}}{Z(C)}} \tag{50}$$

We finally arrive that $T_C^{eff} = T_L$. Similar analysis for the adiabatic process from D to A will give $T_A^{eff} = T_H$. It is, therefore, safe to say that equations (48, 49) are the reversibility conditions for the quantum Carnot cycle.

Let us calculate the extracted work and efficiency of the reversible quantum Carnot cycle. The absorbed and released heat during the isothermal processes A → B and C → D are, respectively, given as

$$Q_H = T_H(S(B) - S(A)) \tag{51}$$

$$Q_L = T_L(S(D) - S(C)) \tag{52}$$

If we employ S(B)=S(C) and S(D)=S(A) for the quantum adiabatic processes, the net extracted work is given as

$$W_C = (T_H - T_L)\big(S(B) - S(D)\big) \tag{53}$$

The heat to work efficiency is $\eta_C = \frac{W_C}{Q_H} = 1 - \frac{T_L}{T_H}$, which is the same as the classical Carnot efficiency. Now, do we impose $\eta_C = 1 - \frac{T_L}{T_H}$ as the highest efficiency for the quantum thermodynamic cycles? The answer is no. Several studies[19,24] showed that quantum heat engines using quantum heat bath, such as a heat bath having entanglement, coherence, squeezing, etc. can be more superior to the classical Carnot cycle. However, as we will prove in the next sections that if the heat bath is classical, $\eta_C = 1 - \frac{T_L}{T_H}$ is the highest for quantum heat engines.

3.8 Quantum Otto Cycle

The quantum mechanical version of the Otto cycle, like its classical version, is comprised of two quantum isochoric and two quantum adiabatic processes. A simple representation of the quantum Otto cycle is schematized in figure (7), where the figure represents the energy values E_n and its populations during the four strokes of the Otto cycle.

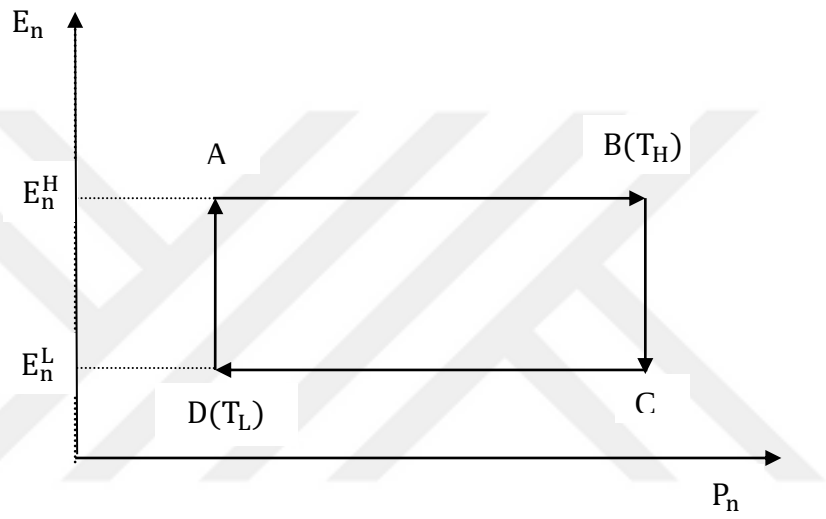

Figure 7. Schematic representation of the quantum Otto cycle which represents the energy levels E_n and its populations P_n during the strokes of the cycle. Here T_H and T_L indicate the hot and cold reservoir temperatures, respectively and E_n^H (E_n^L) represents the level populations during the isochoric heating (cooling) stroke.

The stroke from A (C) to B (D) is the quantum isochoric heating (cooling) process where the working medium is in contact with a hot (cold) heat reservoir at temperature T_H (T_L). According to the quantum mechanical interpretation of the first law of thermodynamic only heat is exchanged, since the energy levels are constant. The exchanged heat is, therefore, equal to the change in the internal energy which can be written for the processes A → B and C → D, respectively, as

$$Q_H = \sum_n E_n^H \left(P_n(B) - P_n(A)\right) \tag{54}$$

$$Q_L = \sum_n E_n^L \left(P_n(D) - P_n(C)\right) \tag{55}$$

The processes from B to C and from D to A are two quantum adiabatic processes where a tuning parameter changes the energy levels quasistatically. According to the quantum adiabatic theorem, the level populations remain unchanged, i.e., $P_n(B) = P_n(C)$ and $P_n(D) = P_n(A)$.

At the end of the isochoric processes, the working medium is in thermal equilibrium with the heat bath. Therefore the local populations at instants B and D are represented by the Gibbs level distribution, i.e., $P_n(B) = {}^{1}/_{Z(B)}\, e^{-\beta_H E_n^H}$ and $P_n(D) = {}^{1}/_{Z(D)}\, e^{-\beta_L E_n^L}$.

The work output is simply given as

$$W = Q_H + Q_L \tag{56}$$

$$= \sum_n (E_n^H - E_n^L)(P_n(B) - P_n(D)) \tag{57}$$

The heat-to-work efficiency is simply given as

$$\eta = \frac{W}{Q_H} \tag{58}$$

$$= \frac{\sum_n (E_n^H - E_n^L)(P_n(B) - P_n(D))}{\sum_n E_n^H (P_n(B) - P_n(D))} \tag{59}$$

The efficiency, as given above, depends on the working medium.

Let us consider a very special working medium where all energy gaps of the working medium change in the same ratio during the adiabatic processes. Please recall that to construct a reversible quantum Carnot cycle, the working medium should possess the above scaling property. This special working medium enables us to compare the quantum Otto and Carnot cycles simply and to show the similarity between the quantum and classical construction of the Otto cycles[1]. For this special working medium, the energy levels should satisfy to the following equation

$$E_n^H - E_m^H = \alpha(E_n^L - E_m^L), \tag{60}$$

where α is the scaling factor which may depend on the system parameters. Let us consider the ground state energy as the reference state, that is $E_0^H = E_0^L = 0$. Therefore, every energy level is scaled as $E_n^H = \alpha E_n^L$. One can easily show that the efficiency in equation (58) can be simplified as $\eta = 1 - 1/\alpha$.

From equation (56), the positive work condition (PWC) is $W > 0$. One can show that this requires $T_H > \alpha T_L$. Using the Otto cycle efficiency η=1-1/α and the PWC condition, one can easily prove that

$$\eta = 1 - \frac{1}{\alpha} < 1 - \frac{T_L}{T_H} \equiv \eta_C \tag{61}$$

That is, the otto cycle efficiency is always smaller than the reversible Carnot cycle efficiency. This is expected because the otto cycle is irreversible. This can also be considered a simple extension of the second law of thermodynamics for quantum systems for this special working medium.

As we remember from the construction of the quantum Carnot cycle, the working medium at the end of the adiabatic stages for this special scaling case defines an effective temperature. Using $E_n^H = \alpha E_n^L$ and the results of the quantum adiabatic theorem, one can easily prove that $T(C) = T_H/\alpha$ and $T(A) = T_L\alpha$ at the instant C and A, respectively. Therefore, the cycle efficiency, in terms of the effective temperatures can be rewritten as

$$\eta = 1 - 1/\alpha \tag{62}$$

$$= 1 - \frac{T(C)}{T_H} = 1 - \frac{T_L}{T(A)} \tag{63}$$

Please recall here that in section (2.2) we have calculated the efficiency of the ideal gas working medium undergoing the classical Otto cycle. It can be seen easily that the classical efficiency, in terms of effective temperature, is equivalent to the quantum efficiency given above in equation (63). Therefore it is safe to tell that the quantum working medium with scalable energy levels in the form $E_n^H = \alpha E_n^L$ has similar properties to that of its classical counterpart using ideal gas as the working medium.

4. IRREVERSIBLE QUANTUM CARNOT CYCLE

In the considered chapter, we explicitly give the general mathematical and thermodynamical description of the quantum version of the classical Carnot cycle for a general quantum working medium[70]. In this formalism, the working medium energy levels are not scalable, therefore the Carnot cycle is irreversible. In figure (8), we simply illustrate such a cycle that has six processes. Here $\langle H \rangle$ is the internal energy and λ denotes the tuning parameter in the working medium which can be controlled externally.

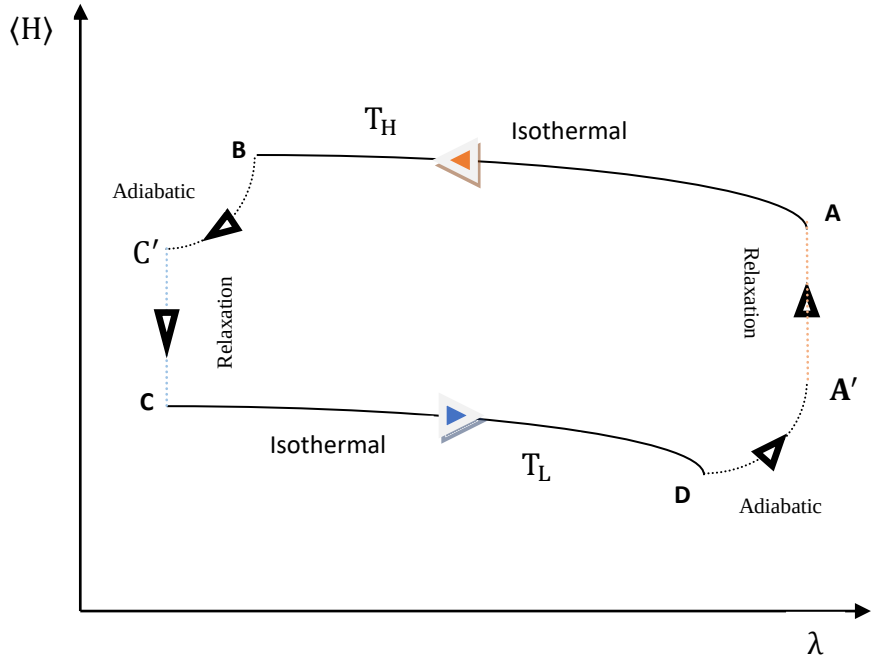

Figure 8. The figure depicts the processes of the irreversible quantum version of the classical Carnot cycle. Please remark here that we consider all stages to be executed quasistatically. In the axes, $\langle H \rangle$ is the internal energy, and λ is the controlled parameter in the working substance, while T_H and T_L represent the absolute temperatures of the hot and cold heat reservoirs, respectively. The explicit thermodynamic explanations of the strokes are given in detail in the main text.

The stroke from A (C) to B (D) is the quantum mechanical version of the isothermal process. Since the process is quasistatic, the working medium is always in equilibrium at the heat bath temperature. Therefore, the occupation levels of the working medium in a quasistatic quantum isothermal process may satisfy the Gibbs distribution which are given as $\frac{1}{Z(i)} e^{-\beta(i)E_n(i)}$ (i = A, B, C, D). Here $Z(i) = \sum_n e^{-\beta(i)E_n(i)}$ is the equilibrium partition function, $E_n(i)$ denote the discrete energy levels of the working medium, $\beta_{A(B)} = \beta_H = (k_B T_H)^{-1}$ and $\beta_{C(D)} = \beta_L = (k_B T_L)^{-1}$ are the inverse temperatures of the heat reservoirs and k_B denotes the Boltzmann constant. In this process, it is safe to use the well-known classical definition $đQ = TdS$ since the quantum mechanical and classical definitions for the quasistatic isothermal process coincide[69].

The stroke from B (D) to C' (A') is regarded as the quantum adiabatic process. In this adiabatic stage, the working substance is removed from the heat bath. The tuning parameter λ is altered between two chosen values. Since the system is closed, the time evolution is governed by the unitary time evolution operator. If the process is quasistatic, the level populations are determined by the quantum adiabatic theorem[1] i.e., $P_n(D) = P_n(A')$ and $P_n(B) = P_n(C')$.

At the instants A' and C', the quantum system may not be in an equilibrium state. Therefore, a relaxation of the working medium is inevitable when the system becomes in touch with the reservoir before the quantum isothermal stage. We here consider that the relaxation occurs at a fixed tuning λ_C (λ_A) during the process $C' \rightarrow$ C ($A' \rightarrow$A). In the end, the working medium is in thermal equilibrium with the heat bath. Only heat is exchanged. The thermalization stages are here regarded as the quantum isochoric processes since the energy levels are invariant[1]. There is no work performed. Therefore, heat is given as the change in the internal energy.

The working medium is in interaction with the hot reservoir during the thermalization process $A' \rightarrow$A which is then encounters a following isothermal process A$\rightarrow$B. The total heat exchanged with the hot bath can be given as

$$Q_H = T_H\big(S(B) - S(A)\big) + \langle H(A)\rangle - \langle H(A')\rangle. \tag{64}$$

Here $\langle H(i)\rangle = \sum_n E_n(i)P_n(i)$ is the internal energy and $S(i) = -k_B \sum_n P_n(i)\ln P_n(i)$ is the entropy at the thermal equilibrium. In a similar

manner, heat is exchanged with the cold bath in the process $C'\rightarrow C$, followed by the process $C \rightarrow D$. It is then given as

$$Q_L = T_L\big(S(C) - S(D)\big) + \langle H(C')\rangle - \langle H(C)\rangle. \tag{65}$$

From the first law of quantum thermodynamics and the conservation of the energy in a cycle, the net work in the six-stroke Carnot cycle (figure 8) is $W_C = Q_H - Q_L$. Then the heat converted to the work efficiency is given by the standard definition $\eta_C = W_C/Q_H = 1 - Q_L/Q_H$.

We now discuss the idea of the total entropy increase of the universe due to the irreversibility in the relaxation steps. Such an analysis will give an attempt to compare the cycle efficiency with the classical Carnot efficiency given by the formula $\eta_C^{ideal} = 1 - T_L/T_H$. The total entropy increase of the universe is the sum of the entropy increases of the reservoir and the working substance. For the thermalization processes $A' \rightarrow A$ and $C' \rightarrow C$, they are given by the following formulas

$$\Delta S^{total}_{A'\rightarrow A} = \big(S(A) - S(D)\big) - \frac{1}{T_H}[\langle H(A)\rangle - \langle H(A')\rangle], \tag{66}$$

$$\Delta S^{total}_{C'\rightarrow C} = \big(S(C) - S(B)\big) - \frac{1}{T_L}[\langle H(C)\rangle - \langle H(C')\rangle]. \tag{67}$$

Please remark here that while writing the above formulas we used the entropy invariance in the quantum adiabatic stages, i.e., $S(C') = S(B)$ and $S(A') = S(D)$. Now by using equations (64), (66), and (67), we can write the irreversible cycle efficiency in terms of the total entropy increase as

$$\eta_C = 1 - \frac{T_L\big(S(B)-S(D)\big)+T_L\Delta S^{total}_{C'\rightarrow C}}{T_H\big(S(B)-S(D)\big)-T_H\Delta S^{total}_{A'\rightarrow A}} \tag{68}$$

The above result is not new which has been recently found also in Reference[47]. Let us give a more intuitive suggestion on equation (68) and give a term called efficiency lag $\mathcal{L}$[14,43,56]. The efficiency lag describes a quantitative difference from the classical Carnot efficiency. Therefore the lag is given by the formula $\eta_C =$

$\eta_C^{ideal} - \mathcal{L}$. Using equation (68) and applying the identity $\frac{(x+a)}{(x-b)} = 1 + \frac{(a+b)}{(x-b)}$, the efficiency lag can be easily found as

$$\mathcal{L} = \frac{\Delta S^{total}_{C'\to C} + \Delta S^{total}_{A'\to A}}{k_B \beta_L Q_H}. \tag{69}$$

Equation (69) shows that the efficiency lag is the function of the total entropy increases of the universe in the two irreversible relaxation processes. According to the second law of classical thermodynamics, the total entropy increase of the universe is a nonnegative quantity[47]. Therefore, the efficiency (equation (68)) in terms of the total entropy increases should be lower than the classical Carnot efficiency [47]. However, this strong insight has not a direct evidence in quantum thermodynamics. Here we prove that the entropy increase in equation (67) and the efficiency lag in equation (69) are always greater than zero for the irreversible processes. When we use the properties of the notion called quantum relative entropy[63], and after some straightforward algebra as given in Appendix, we directly obtain the following equations,

$$\Delta S^{total}_{C'\to C} = k_B S(\rho_{C'} || \rho_C), \tag{70}$$

$$\Delta S^{total}_{A'\to A} = k_B S(\rho_{A'} || \rho_A). \tag{71}$$

Here $S(\rho||\sigma) = tr(\rho ln\rho - \rho ln\sigma)$ denotes the quantum relative entropy[63] and ρ_j are the density matrices at the points j of the cycle in figure 8. Using the above relation (equation (71)), the efficiency lag in equation (69) can also be given as

$$\mathcal{L} = \frac{S(\rho_{C'} || \rho_C) + S(\rho_{A'} || \rho_A)}{\beta_L Q_H} \tag{72}$$

Klein's inequality[63] states that the quantum relative entropy is nonnegative, i.e., $S(\rho||\alpha) \geq 0$; when $\rho = \sigma$, it is zero. Therefore, we fulfill the statement of the second law for the quantum mechanical systems as well as we prove that the total entropy increase and consequently efficiency lag are always non-negative quantities.

Please remark here that the lag is the consequence of the irreversible thermalization strokes as denoted in figure (8). It directly measures the detrimental role of the relaxation strokes on the cycle efficiency which is formulated in terms of its microscopic (density matrix) state dynamics. Note that the reversible cycle efficiency is system parameter independent given by the classical Carnot efficiency $1-\mathrm{T_L}/\mathrm{T_H}$. On the contrary, the irreversible cycle efficiency in equation (68) is highly system-dependent as determined by the efficiency lag $\mathcal{L}$. Similar attempts to derive an efficiency lag have also been given for the quantum Otto cycle[14,43]. In the studies[14,43] the lag accounts for the irreversibility both due to the finite-time adiabatic and the isochoric stages.

The reversibility of the quantum Carnot cycle for a general quantum working medium has been previously discussed in the text (see Sec. 2.5). Let us recall the concept once more again. The Carnot cycle is reversible if the energy levels satisfy certain scalability conditions. More explicitly, if the energy gap change satisfies the following equations

$$\mathrm{E_n(A)}-\mathrm{E_m(A)}=\frac{\mathrm{T_H}}{\mathrm{T_L}}[\mathrm{E_n(D)}-\mathrm{E_m(D)}], \tag{73}$$

$$\mathrm{E_n(B)}-\mathrm{E_m(B)}=\frac{\mathrm{T_H}}{\mathrm{T_L}}[\mathrm{E_n(C)}-\mathrm{E_m(C)}], \tag{74}$$

then the Carnot cycle is said to be reversible[1]. Under the above conditions, the instants A' and C' are thermal states at the reservoir temperatures. In other words, the states A' and A as well as C' and C are indistinguishable. There is no entropy increase in the universe (equation (67)). Therefore, the lag in equation (69) is also null. The cycle efficiency then coincides with the classical Carnot efficiency.

4.1 Working Substance-Two Interacting Spins 1/2

In this section we propose two interacting spins $1/2$ as the working substance of the above discussed irreversible Carnot cycle. We will mainly explore the role of quantum interactions between the spins which seems a term that breaks down the scalability in equations (73) and (74) is responsible for the Carnot cycle to be irreversible**.**

In order to understand the nature of irreversibility in the quantum Carnot cycle and the role of quantum coupling on the cycle operation, let us first discuss a single spin $1/2$ and two uncoupled spins $1/2$ as the working medium. The Hamiltonian for the single spin $1/2$ can be written as, $\mathrm{H} = \frac{1}{2}\lambda\sigma_{\mathrm{Z}}$, where $\lambda = \hbar\omega$ is assumed as the tuning parameter through the cycle, $\hbar$ is the Planck constant, ω is the frequency and σ_{Z} is the Pauli matrix. In order to tune the parameter λ, one should simply change the external magnetic field. There is only one energy gap, therefore the system is scalable. If we choose λ as $\lambda_A = (T_H/\mathrm{T_L})\lambda_D$ and $\lambda_C = (T_L/\mathrm{T_H})\lambda_B$ at the end of the adiabatic processes, then scalability in equations (73) and (74) can be fulfilled. Therefore, under the above changes, the efficiency is equal to the classical Carnot efficiency. The extension to the two spins $1/2$ case can be given by the Hamiltonian $H = \frac{1}{2}\lambda(\sigma_{\mathrm{Z}}^1 + \sigma_{\mathrm{Z}}^2)$. If one applies the above proposed adiabatic changes as $\lambda_A = (T_H/\mathrm{T_L})\lambda_D$ and $\lambda_C = (T_L/\mathrm{T_H})\lambda_B$, then one can obtain the reversible cycle with operational efficiency $\eta_{\mathrm{C}} = 1 - \mathrm{T_L}/\mathrm{T_H}$.

Now let us consider inherent and controllable interactions between the spins that exist. Here we model the interaction term in the Hamiltonian via the transverse field Ising model. The Hamiltonian can be given as[64]

$$\mathrm{H} = \frac{1}{2}\lambda(\sigma_{\mathrm{Z}}^1 + \sigma_{\mathrm{Z}}^2) + \mu\sigma_{\mathrm{X}}^1\sigma_{\mathrm{X}}^2. \tag{75}$$

Here μ is the strength of quantum interactions which is anti-ferromagnetic, i.e., $\mu > 0$. The eigenvalues are easily computable which are listed as $\{-\mu, \mu, -\sqrt{\lambda^2 + \mu^2}, \sqrt{\lambda^2 + \mu^2}\}$. Here we consider λ is the only parameter that is changed between the given values in the cycle that is, $\lambda_A \to \lambda_B \to \lambda_C \to \lambda_D \to \lambda_A$,

and $\lambda_A = (T_H/T_L)\lambda_D$ and $\lambda_C = (T_L/T_H)\lambda_B$. Using the eigenvalues and the proposed changes, it can be shown that the scalability in equations (73) and (74) is not satisfied. Therefore, the states at the instants A' and C' are not thermal states. It can be then regarded the quantum cycle is irreversible.

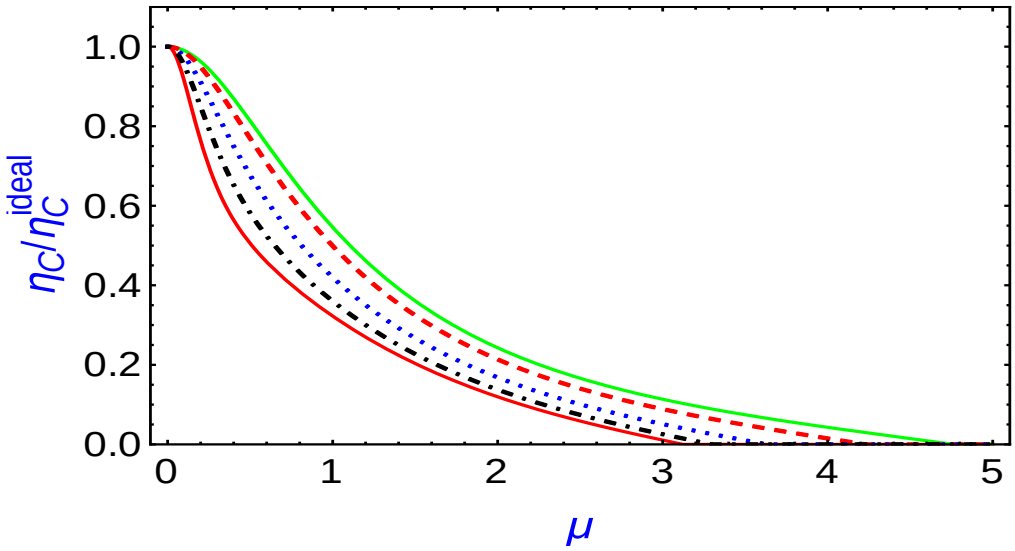

Figure 9. The ratio $\frac{\eta_C}{\eta_C^{ideal}}$, where the efficiency is divided to the classical efficiency, as a function of coupling strength μ for the temperatures $T_H = 2.0$ and $T_L = 1.0$ and for the fixed tuning parameter $\lambda_D = 1.0$. The (green-solid, red-dashed, blue-dotted, black-dot dashed, red-solid) lines are for $\lambda_B = (1.4, 1.6, 1.8, 1.9, 1.95)$ respectively. Here and in the following figures, we set $\hbar = k_B = 1$ (dimensionless units).

Please recall again that the quantum interactions between the spins are the key quantity that is responsible for the cycle irreversibility which breaks down the scale invariance. Therefore, we ask ourselves how the cycle mode and the performance outputs are affected by the quantum coupling strength. In figure 9, we depict the ratio η_C/η_C^{ideal}, where the efficiency is divided to the classical Carnot efficiency, as a function of the interaction strength μ for the temperatures $T_H = 2.0$ and $T_L = 1.0$ and for different λ_B values. Note that when μ= 0, the ratio $\frac{\eta_C}{\eta_C^{ideal}} = 1$. From figure 9 we found a dramatic decrease in the cycle efficiency due to the quantum interactions. Here, the cycle efficiency decays to zero as a function

of μ. One may easily remark that the lag has given in equation (72) increases as a function of quantum interaction. In this thesis, we adopt the total entropy increase in the universe as a quantification of the irreversibility in the proposed quantum Carnot cycle which is depicted in figure (10). The figure shows that the irreversibility does not necessarily increase when the coupling between the spins increases. Figure (10) shows that the total entropy has a non-monotone

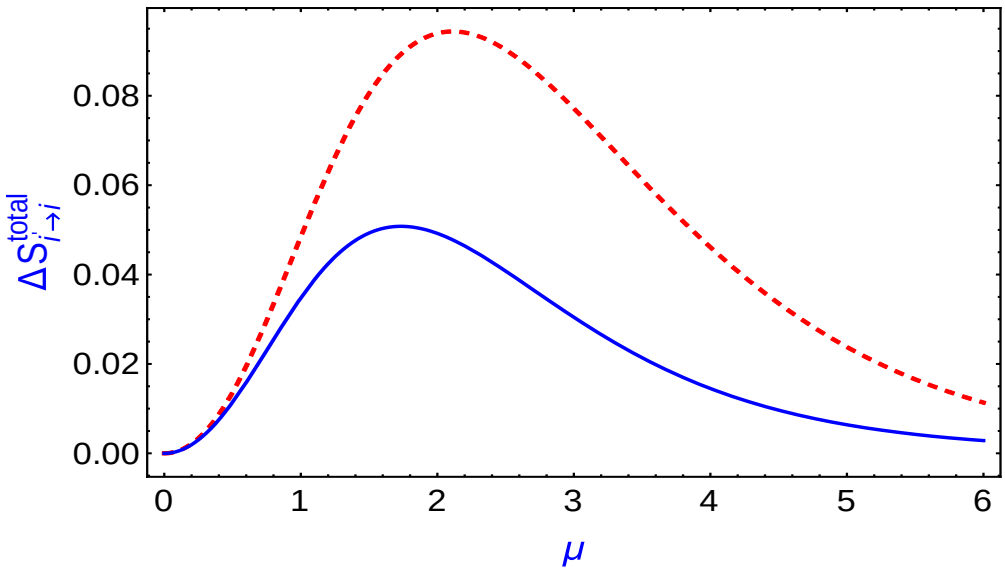

Figure 10. The total entropy increases given in equations (66) and (67), i.e., $\Delta S^{total}_{A'\to A}$(solid line) and $\Delta S^{total}_{C'\to C}$(dashed line) versus μ for the temperatures $T_H = 2.0$ and $T_L = 1.0$ and the for tuning parameters $\lambda_D = 1.0$ and $\lambda_B = 1.6$.

behavior as a function of μ; they have single maximums at certain μ which increase until the maximums and then exponentially decay as a function of μ. The heat engine character exists only for a limited range of interaction strength values (see figure 9 again). Note that the interaction strength range in which the cycle harvests positive work decreases as the parameter λ_B increases. As a final remark of figure, the efficiency is higher for a smaller λ_B value at a given interaction strength.

As the second figure of merit of the quasistatic irreversible cycle, we consider the work output. To compare the work output of the reversible and irreversible cycle cases and to reveal the impact of the coupling between spins on the harvested work, we plot the ratio $W_C/W_C^{\mu=0}$ versus μ in figure (11). Note that $W_C^{\mu=0}$ indicates the work harvested from the non-interacting spins (where $\mu = 0$) in which the energy levels are scalable and therefore the cycle is thermodynamically reversible. When $W_C/W_C^{\mu=0} > 1$, we regard the quantum interaction enhances the harvested work. Figure (11) shows that the quantum coupling can significantly enhance the harvested work over the one produced by the non-interacting spins. This unusual behavior can be explained as follows. For the case of the interacting spin, levels having higher energies may contribute to the harvested work. Such energy levels can be responsible for the irreversible cycle to harvest more positive work than the reversible cycle can do. In figure (11), we alter the magnetic field at instant B (i.e., λ_B) and elucidate its role. We found here that for a larger λ_B, the cycle can be more capable to produce positive work over the uncoupled (reversible) one. Let us give special attention to the value $\lambda_B = 1.95$, where $W_C/W_C^{\mu=0} \approx 3.8$ in the vicinity of $\mu = 1$ and $W_C/W_C^{\mu=0} > 1$ could be possible in the region $0 < \mu < 2.5$. When the magnetic field value at instant B becomes smaller, $W_C/W_C^{\mu=0}$ ratio and the interaction strength range where $W_C/W_C^{\mu=0}$ are greater than zero becomes smaller. As also given in figure (9), the cycle produces work only for a limited range of coupling strength where it becomes zero after a further increase of interaction strength. In the negative work region, we have $Q_L > Q_H > 0$ in which we regard it has no industrial implementations.

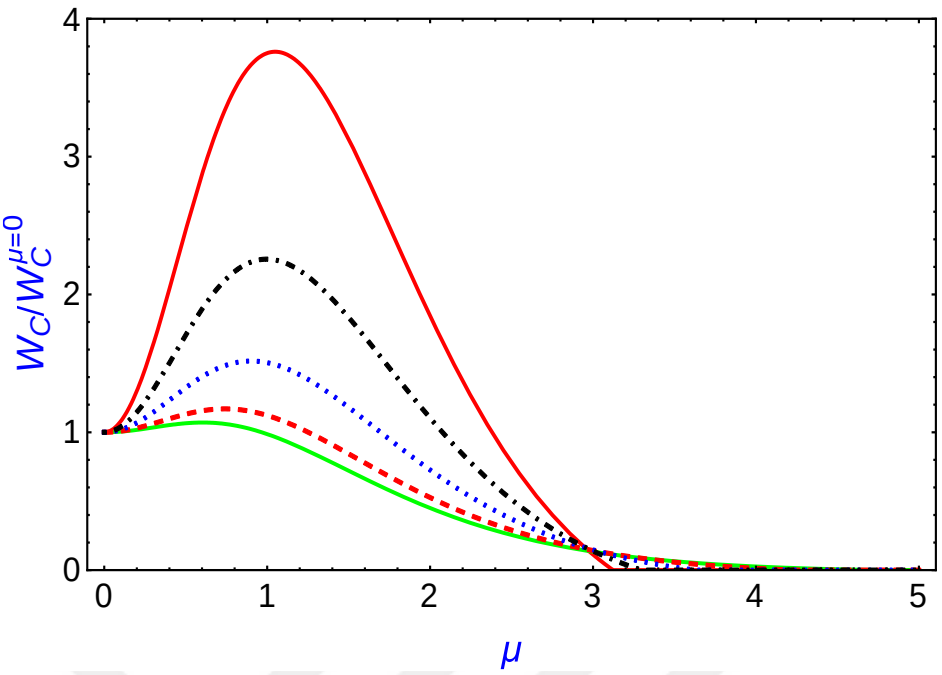

Figure 11. Work produced by the interacting spins divided by the work produced by the non-interacting spins, i.e., $W_C/W_C^{\mu=0}$ versus coupling strength μ for the same parameters and line labels as given in figure (9).

A natural question arises. How one can construct a reversible cycle for the coupled spins case. In this scenario, one should tune the interaction strength and the magnetic field simultaneously during the strokes of the cycle. If one is able to ensure the proportionality $\frac{\mu_i}{\lambda_i} = r$ (where r should be a constant) at the instants of the cycle and sets the magnetic field in such a way $\lambda_A = (T_H/T_L)\lambda_D$ and $\lambda_C = (T_L/T_H)\lambda_B$ at the end of the adiabatic strokes, then the scalability in equations (73,74) could be satisfied for the interacting spins given in equation (75). Then the cycle is reversible producing work at the efficiency, $\eta_C = 1 - T_L/T_H$. One could show that enhancing work output via quantum interactions can still be possible[34,61].

5. CONCLUSIONS AND RECOMMENDATIONS

In this thesis, we have given a comprehensive analysis for the extension of the thermodynamic laws, thermodynamic processes, and Otto and Carnot cycles to the quantum domain. We have shown that quantum mechanics can put some limits on such extensions. For instance, by using two spins 1/2 interacting through isotropic Heisenberg XXX interaction and embedded in a heat bath, we have proven that the zeroth law of thermodynamics cannot be directly extended to the quantum domain due to the lack of any temperature operator. In this example, even though the combined system (two spins and the bath) is in thermal equilibrium, the spins individually have been found to be at different effective temperatures. Full quantum mechanical formulation of the Carnot cycle has been given for a general quantum system which is irreversible unless the energy levels are scalable. The efficiency of the cycle is connected to the quantum relative entropy and shown to be always smaller than the classical Carnot efficiency fulfilling the second law.

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7. APPENDICES

Here we prove the formulas obtained in equations (70,71). Using Boltzmann-Gibbs distribution given as $P_n(i) = {}^{1}/_{Z(i)}\, e^{-\beta(i)E_n(i)}$, the entropy at thermal points can be rewritten in the form as

$$S(i) = -k_B \sum_n P_n(i) \ln P_n(i) \tag{76}$$

$$= k_B \beta_i \sum_n P_n(i) E_n(i) + k_B \sum_n P_n(i) \ln Z(i) \tag{77}$$

$$= k_B \beta_i \langle H(i) \rangle + k_B \ln Z(i), \tag{78}$$

where $\beta_A = \beta_B = (k_B T_H)^{-1} \equiv \beta_H$ and $\beta_C = \beta_D = (k_B T_L)^{-1} \equiv \beta_L$. Using the result in equation (78), the total entropy increase given in equation (66,67) can be written in the form as

$$\Delta S^{total}_{C' \to C} = k_B [\ln Z(C) - \ln Z(B) + \beta_L \langle H(C') \rangle - \beta_H \langle H(B) \rangle], \tag{79}$$

$$\Delta S^{total}_{A' \to A} = k_B [\ln Z(A) - \ln Z(D) + \beta_H \langle H(A') \rangle - \beta_L \langle H(D) \rangle]. \tag{80}$$

Now let us prove that equations (79,80) is equal to the quantum relative entropy between density operators obtained at the end of the adiabatic and the thermalization states. First consider the process $B \to C' \to C$, where the relative entropy is

$$S(\rho_{C'} || \rho_C) = tr(\rho_{C'} \ln \rho_{C'}) - tr(\rho_{C'} \ln \rho_C). \tag{81}$$

The first term on the right-hand side of the equation is equal the von Neumann entropy at instant C' which does not change under unitary evolution. We can write it as

$$tr(\rho_{C'} \ln \rho_{C'}) = -S(B)/k_B \tag{82}$$

$$= -\beta_H \langle H(B) \rangle - \ln Z(B). \tag{83}$$

Using the eigen spectrum of the Hamiltonian $H(i) = \sum_n E_n(i) |n(i)\rangle\langle n(i)|$ and the density operator $\rho_i = \sum_n P_n(i) |n(i)\rangle\langle n(i)|$, the second term on the right hand side of equation (81) can be rewritten as,

$$\mathrm{tr}(\rho_{C'}\ln\rho_C) = \mathrm{tr}(\rho_{C'}\sum_n \ln P_n(C)|n(C)\rangle\langle n(C)|) \quad (84)$$

$$= \sum_n \ln P_n(C)\langle n(C)|\rho_{C'}|n(C)\rangle \quad (85)$$

$$=\sum_n[-\beta_L E_n(C) - \ln Z(C)]\langle n(C)|\rho_{C'}|n(C)\rangle \quad (86)$$

$$= -\beta_L\langle H(C')\rangle - \ln Z(C). \quad (87)$$

Therefore, we obtain the result at the end,

$$S(\rho_{C'}||\rho_C) = \ln Z(C) - \ln Z(B) + \beta_L\langle H(C')\rangle - \beta_H\langle H(B)\rangle. \quad (88)$$

One can apply a similar procedure to calculate the relative entropy $S(\rho_{A'}||\rho_A)$. We directly write the result which is

$$S(\rho_{A'}||\rho_A) = \ln Z(A) - \ln Z(D) + \beta_H\langle H(A')\rangle - \beta_L\langle H(D)\rangle. \quad (89)$$

If one compares equations (79) and (80) with equations (88) and (89), the equalities can be written which are

$$\Delta S^{\mathrm{total}}_{C'\to C} = k_B S(\rho_{C'}||\rho_C), \quad (90)$$

$$\Delta S^{\mathrm{total}}_{A'\to A} = k_B S(\rho_{A'}||\rho_A). \quad (91)$$

According to the Klein's inequality[63], $\Delta S^{\mathrm{total}}_{C'\to C}$ and $\Delta S^{\mathrm{total}}_{A'\to A}$ are always greater than zero or equal to zero.