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**A possible inadequacy of a recent proposal for redefining
heat and work in quantum thermodynamics**

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EDUARDO BORGES BOTTOSSO

A possible inadequacy of a recent proposal for redefining heat and work in quantum thermodynamics

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ATA DE DEFESA DE DISSERTAÇÃO

Ata nº 191 da sessão de Defesa de Dissertação de Eduardo Borges Bottosso, que confere o título de Mestre em Física, na área de concentração em Física.

Aos 15 dias do mês de março de 2021, a partir das 14h30min, por meio de videoconferência, realizou-se a sessão pública de Defesa de Dissertação intitulada "A possible inadequacy of a recent proposal for redefining heat and work in quantum thermodynamics". Os trabalhos foram instalados pelo Orientador, Professor Doutor Norton Gomes de Almeida (IF/UFG), com a participação dos demais membros da Banca Examinadora: Professor Doutor Miled Hassan Youssef Moussa (IFSC/USP), membro titular externo; e Professor Doutor Lucas Chibebe Céleri (IF/UFG), membro titular interno. Durante a arguição, os membros da banca não fizeram sugestão de alteração do título do trabalho. A Banca Examinadora reuniu-se em sessão secreta a fim de concluir o julgamento da Dissertação, tendo sido o candidato aprovado pelos seus membros. Proclamados os resultados pelo Professor Doutor Norton Gomes de Almeida, Presidente da Banca Examinadora, foram encerrados os trabalhos e, para constar, lavrou-se a presente ata que é assinada pelos Membros da Banca Examinadora, aos 15 dias do mês de março de 2021.

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Resumo

Resumo A primeira identificação de um sistema quântico aberto como um modelo para um motor térmico quântico data de 1959. Desde então, a física não tem um conjunto concreto de fórmulas para definir, com precisão, como lidar com o calor e trabalhar no contexto de conjuntos quânticos. Uma das propostas mais proeminentes, que foi afirmada pelo artigo de R. Alicki de 1979, tem um regime de validade limitado e pode levar a algumas inconsistências com relação à primeira lei da termodinâmica. Várias abordagens para o problema foram propostas, levando a um novo conjunto de definições para calor e trabalho em termodinâmica quântica. Particularmente, novas redefinições para calor e trabalho foram introduzidas, as quais são baseadas na entropia de von Neumann. Nosso objetivo aqui é apresentar essa nova formulação, bem como sua motivação e investigar as consequências dessas fórmulas. Estudamos alguns modelos simples que empregam esse novo conjunto de definições. Nossa análise mostra um comportamento peculiar dos sistemas quânticos quando esse novo formalismo é dado como certo, possivelmente indicando uma inadequação dessas novas definições.

Palavras-chave: sistemas quânticos abertos. termodinâmica quântica. definições para calor e trabalho.

Abstract

The first identification of an open quantum system as a model for a quantum thermal engine dates back to 1959. Since then physics doesn't have a concrete set of formulas to define, precisely, how to address heat and work in the context of quantum ensembles. One of the most prominent proposals, which was stated by R. Alicki 1979's paper, has a limited regime of validity and can lead to some inconsistencies with regards to the first law of thermodynamics. Several approaches to the problem have been proposed, leading to some new set of definitions for heat and work in quantum thermodynamics. Particularly, new redefinitions for heat and work have been introduced, which are based on von Neumann entropy. Our goal here is to present this new formulation as well as its motivation and to investigate the consequences of these formulas. We study some simple models employing this new set of definitions. Our analysis shows a peculiar behavior of quantum systems when this new formalism is taken for granted, possibly indicating an inadequacy of these new definitions.

Keywords: open quantum system. quantum thermodynamics . definitions for heat and work.

Sumário

1	INTRODUCTION	9
2	FUNDAMENTAL CONCEPTS AND RELEVANT MATHEMATI- CAL TOOLS	11
2.1	The von Neumann Entropy	11
2.2	Markovian Quantum Master Equation	12
2.3	Density operator	19
3	PROPOSAL FOR “REFINED” OR “UNAMBIGUOUS” HEAT AND WORK DEFINITIONS IN QUANTUM THERMODYNAMICS . . .	21
4	RESULTS AND DISCUSSIONS	25
4.0.1	Two Qubits dephasing interaction	25
4.0.2	Two level atom in contact with a heat bath at zero temperature	31
5	CONCLUSIONS	37
	REFERÊNCIAS	39

1 Introduction

Quantum Thermodynamics is concerned, among other things, with the study of energy exchange between quantum ensembles. With the aid of the formalism by John von Neumann (1) one can describe such ensembles of quantum states, thus enabling thermodynamics ideas to be applicable on any scale.

The first quantum heat engine was presented in the paper by H.E.D Scovil and O. Schulz-DuBois (2), where they identified the three level system as the working substance of the machine acting between two baths at different temperatures. In maser regime, they found that the thermodynamic efficiency was smaller than the Carnot's. One could ask how small can a heat machine be. Linden et al. (3) investigated this matter and proposed to characterize the “size” of the machine as the number of dimensions of the Hilbert space used to characterize the system employed as the working substance and found that there is no difficulty in constructing, for example, an refrigerator constituted by two qubits.

Quantum heat machines are not the only goal of quantum thermodynamics investigations. In fact, the scope of this theory also embraces non-equilibrium phenomena. We can summarize some of the branches of investigations concerned with quantum thermodynamics: quantum heat machines (4, 5, 6), fluctuation relations (7), autonomous quantum clocks, one-shot statistical mechanics (8), algorithmic cooling (9, 10), applications of contextuality (11), non-markovianity (finite-size baths) (12), thermodynamics uncertainty relations (13), resource theories for thermodynamics (14, 15), etc.

In this work we are most concerned about the investigation of the definitions of heat and work in quantum thermodynamics. The importance to have a consistent theory to define these quantities in quantum domain is of fundamental and also practical character, once it is closely related to the first law of thermodynamics and intimately related to quantum engines applications.

In 1979 the seminal paper of Alicki (16) set the first definitions of heat and work for quantum thermodynamics:

$$E_A(t) = \langle H_A(t) \rangle \equiv \text{Tr} \{ \rho_A(t) H_A(t) \}, \quad (1.1)$$

$$d \langle Q_A(t) \rangle \equiv \text{Tr} \{ d\rho_A(t) H_A(t) \}, \quad (1.2)$$

$$d \langle W_A(t) \rangle \equiv \text{Tr} \{ \rho_A(t) dH_A(t) \}. \quad (1.3)$$

Notice that it came naturally from the identification of the internal energy of the system as the expected value of the Hamiltonian operator over the state of the system.

R. Alicki set one of the first correspondences between an open quantum system and a model of quantum heat engine. The physical context of his work is situated in the

limiting case where the system of interest is weakly coupled with the environment and is subjected by slowly varying external conditions.

In fact these definitions can lead to physical inconsistencies when applied indiscriminately, such as violation of the first law of thermodynamics. We will discuss this matter in the example of the dephasing interaction between two qubits in Section 4.0.1.

After Alicki's work, appeared some new proposals for generalizing the concepts of heat and work in quantum thermodynamics. Bera et al. (17) proposed a formalism based on the information-theoretic approach that can also deal with strong quantum correlations between the system and the bath.

Another recent proposal from Ahmadi et al. (18) and, independently, by Alipour et.al (19), pointed out that Alicki's formulation is not very precise because it does not consider the portion of work that can be transferred to the system via interaction with the environment. They proposed a new set of definitions based on the "trajectory" taken by the density operator of the system of interest, identifying, for short, as heat the portion of energy transferred that accounts for entropy (von Neumann's) change. In chapter 4 we are going to investigate in details this proposal via some applications in two simple examples.

2 Fundamental concepts and relevant mathematical tools

This chapter was designed to present a short introduction to some key concepts and mathematical foundations that we are going to use throughout this work. This chapter was not intended to exhaust the subjects, but rather to give some cohesive character to the present work.

2.1 The von Neumann Entropy

In the core of the formulation that we are just going to present lies the von Neumann entropy. Among other things, it is a measure of how mixed an ensemble is, and thus it is a function of the density operator. We are going to present, or justify, the form of this entropy and it will become clear why the majority of works on quantum thermodynamics consider this as the relevant entropy.

We are interested in finding an entropy functional $S(\rho)$ that can quantify how mixed a state is. We demand that this mathematical object satisfies some requirements:

i) $S(\rho) = 0 \leftrightarrow \rho$ is pure;

ii) $S(U^\dagger \rho U) = S(\rho) \rightarrow S(\rho) = \text{Tr}\{F(\rho)\}$: $S(\rho)$ is invariant under similarity transformation;

iii) $S(\rho_{AB}) = S(\rho_A) + S(\rho_B)$ for A and B being independent.

In the above statements, (i) is saying that a pure ensemble has no uncertainty, once one knows ρ exactly; (ii) implies that the functional S should be independent of the choice of basis, therefore depending only on the eigenvalues of ρ , so S can be written as the trace of some function of ρ ; (iii) states that for an uncorrelated system, $\rho_{AB} = \rho_A \otimes \rho_B$, the entropy of the combined system is equal to the sum of the entropy of the individuals, so it is extensive.

From the property (ii) we can write,

$$S = \text{Tr}\{F(\rho)\}. \quad (2.1)$$

Calling $F = \rho g(\rho)$ where $g(\rho)$ is an hermitian operator, we find

$$S = \text{Tr}\{\rho g(\rho)\} \equiv \langle g(\rho) \rangle, \quad (2.2)$$

i.e., the entropy is the expected value of an hermitian operator which is a function of the state of the system. Now, from the property (iii) we can write:

$$\langle g(\rho_A \otimes \rho_B) \rangle = \langle g(\rho_A) \rangle + \langle g(\rho_B) \rangle, \quad (2.3)$$

$g(\rho)$ should have the form of the logarithmic function, once the expected value of the composite system is equal to the sum (just remember that the log of a multiplication is the sum of the logs). Therefore we end-up with the following formula

$$S = -Tr\{\rho \ln \rho\}, \quad (2.4)$$

where the minus sign was inserted to guarantee the non-negativity of S ; the above formula is the well-known von Neumann entropy.

Some natural questions arises: what is the relationship between the above formula with thermodynamics? Which density matrix has the largest entropy given that we fixed $\langle H \rangle$? In other words, we want to maximize $S(\rho)$ given that $E = \langle H \rangle = Tr\{\rho H\} = \text{constant}$ and $Tr\{\rho\} = 1$. A very useful method to solve this kind of problem is the Lagrange Multipliers (20). To this end we define a new function S' to which we add two unknowns coefficients that multiplies the constraints:

$$S' = -Tr\{\rho \ln \rho\} - \beta(Tr\{\rho H\} - E) - \gamma(Tr\{\rho\} - 1)$$

by varying $\rho \rightarrow \rho + \delta\rho$ we can expand the above expression and make the term linear in $\delta\rho$ equal to zero:

$$0 = Tr\{-\delta\rho \ln \rho - \rho \frac{1}{\rho} \delta\rho - \beta H \delta\rho - \gamma \delta\rho\}$$

in order for this expression to be true, we need

$$\begin{aligned} \ln \rho &= -\beta H - \gamma - 1 \\ \rho &= e^{-\beta H} e^{-\gamma-1} \\ \rho &= \frac{e^{-\beta H}}{Z(\beta)} \end{aligned} \quad (2.5)$$

where $Z(\beta) = e^{-\gamma-1} = Tr\{e^{-\beta H}\}$ is the partition function; β is fixed by $\langle H \rangle = Z(\beta)^{-1} Tr\{H e^{-\beta H}\} = E$; the coefficient β can be shown to be $\frac{1}{k_B T}$, where k_B is the Boltzmann constant.

So, by maximizing the entropy given by Eq. (2.4) with the constraints of fixed total energy and that of trace-preserving, we ended-up with a ρ that is the quantum version of Boltzmann distribution, characterizing an quantum ensemble with finite temperature, i.e. in thermal equilibrium with a bath characterized by $\beta = \frac{1}{k_B T}$.

2.2 Markovian Quantum Master Equation

In the real physical situations nothing is perfectly hermetic. So, quantum physical states are always interacting with its environment. Then one would ask how does this

system, which is an open system, evolves in time? In this section we are going to present the fundamental theory that deals with this problem.

We are going to present a derivation of the master equation from first principles to treat the system-environment interaction (21, 22). The total Hamiltonian reads

$$\hat{H} = \hat{H}_S + \hat{H}_E + \alpha \hat{H}_{int}, \quad (2.6)$$

where α is the parameter of interaction and $\hat{H}_S, \hat{H}_E, \hat{H}_{int}$ are the system, environment and interaction Hamiltonians, respectively. In the interaction picture, the evolution of the total system density operator is given by the Liouville-von Neumann equation:

$$\frac{d}{dt} \hat{\rho}_{Total} = -\frac{i}{\hbar} \alpha [\hat{H}_{int}(t), \hat{\rho}_T(t)], \quad (2.7)$$

where $\hbar$ is the reduced Planck's constant. By integrating the above formula,

$$\hat{\rho}_T(t) = \hat{\rho}_T(0) - \frac{i}{\hbar} \alpha \int_0^t ds [\hat{H}_{int}(s), \hat{\rho}_T(s)]. \quad (2.8)$$

Now, iterating two times, i.e. substituting Eq. (2.8) into Eq. (2.7). We find:

$$\frac{d}{dt} \hat{\rho}_T(t) = -i\alpha [\hat{H}_{int}(t), \hat{\rho}_T(0) - \frac{i}{\hbar} \alpha \int_0^t ds [\hat{H}_{int}(s), \hat{\rho}(s)]], \quad (2.9)$$

$$= -\frac{i}{\hbar} \alpha [\hat{H}_{int}(t), \hat{\rho}_T(0)] - \frac{\alpha^2}{\hbar} \int_0^t ds [\hat{H}_{int}(t), [\hat{H}_{int}(s), \hat{\rho}(s)]], \quad (2.10)$$

$$= -\frac{i}{\hbar} \alpha [\hat{H}_{int}(t), \hat{\rho}_T(0)] - \frac{\alpha^2}{\hbar} \int_0^t ds [\hat{H}_{int}(t), [\hat{H}_{int}(s), \hat{\rho}(t)]] + O(\alpha^3) + \dots \quad (2.11)$$

Here we are going to truncate to the second order on alpha. This is our first approximation, i.e. we are considering alpha, the interaction strength, a small number.

We are interested in obtaining the equation of motion for the system of interest. Tracing out the degrees of freedom of the environment, we obtain the following equation:

$$\begin{aligned} \frac{d}{dt} \hat{\rho}_S(t) &= Tr_E \left\{ \frac{d}{dt} \hat{\rho}_T(t) \right\} \\ &= -\frac{i}{\hbar} \alpha Tr_E \{ [\hat{H}_{int}(t), \hat{\rho}_T(0)] \} - \frac{\alpha^2}{\hbar} \int_0^t ds Tr_E \{ [\hat{H}_{int}(t), [\hat{H}_{int}(s), \hat{\rho}(t)]] \}. \end{aligned} \quad (2.12)$$

In fact this formula describes all the exchange of information between the system (from now on we refer to the system of interest as simply by “system”) and the environment between 0 and t . So, in the most general form, by realizing the trace over E , the integrand can be written as

$$\int_0^t ds \kappa_{(s-s')} [\hat{\rho}_S], \quad (2.13)$$

where the term $\kappa_{(s-s')}$ is called the memory kernel, which is effectively a map acting on the state of the system which can account for the system-environment exchange of information, although it may be very complicated. Fortunately, to our purposes, in most cases we are

going to deal with memory-less scenarios where this kernel turns out to be a delta function. This is the case for the so-called Markov approximation. And we can set the upper limit of integration as infinity without any loss.

In order to obtain the equation of motion for the system, we have to look at the physical problem and propose some approximations and to state some mathematical facts:

- i) Here we are going to make the following approximation: $\hat{\rho}_T(t) = \hat{\rho}_S(t) \otimes \hat{\rho}_E(t)$. Note that this procedure is suggesting that there is no correlation between the system and the reservoir, which is not true. Since this approach greatly simplifies the calculations and leads to the same results, we will do it;
- ii) $\hat{\rho}_E(0) = \hat{\rho}_E(t) = \frac{e^{-\beta \hat{H}_E}}{Z(\beta)}$, i.e. the bath starts at the thermal state and remains there. It happens because the characteristic time scale for the relaxation of the bath is way faster than the typical time in which the system changes ;
- iii) $\hat{H}_I = \sum_i \hat{S}_i \otimes \hat{E}_i$: one can represent, without loss of generality, the interaction Hamiltonian as the sum of the tensor product of system's and environment's operators.

With the aid of the above statements, the first term of Eq. (2.12) can be written as:

$$\begin{aligned}
 &= -\frac{i}{\hbar} \alpha \text{Tr}_E \{ [\hat{H}_I(t), \hat{\rho}_T(0)] \}, \\
 &= -\frac{i}{\hbar} \alpha \text{Tr}_E \{ \sum_i \hat{S}_i \otimes \hat{E}_i, \hat{\rho}_S(0) \otimes \hat{\rho}_E(0) \}, \\
 &= -\frac{i}{\hbar} \alpha \sum_i \left(\hat{S}_i(t) \hat{\rho}_S(0) \otimes \text{Tr}_E \{ \hat{E}_i \hat{\rho}_E(0) \} - \hat{\rho}_S(0) \hat{S}_i(t) \otimes \text{Tr}_E \{ \hat{\rho}_E(0) \hat{E}_i(t) \} \right),
 \end{aligned}$$

where $\langle E_i \rangle_0 = \text{Tr}_E \{ \hat{E}_i \hat{\rho}_E(0) \} = 0$.

So far our equation of motion for the system S reads

$$\frac{d}{dt} \hat{\rho}_S(t) = -\frac{\alpha^2}{\hbar} \int_0^\infty ds \text{Tr}_E \{ [\hat{H}_{int}(t), [\hat{H}_{int}(s), \hat{\rho}(t)]] \}. \quad (2.14)$$

But the above equation can lead to some physical inconsistencies, i.e. it is not a completely positive dynamics. To deal with that we employ a superoperator $\hat{H}$ that has a complete set of eigenoperators in which we can expand the system's operators:

$$\hat{S}_i = \sum_\nu \hat{S}_i(\nu). \quad (2.15)$$

These eigenoperators respects the following commutation relations:

$$[\hat{H}, \hat{S}_i(\nu)] = -\nu \hat{S}_i(\nu), \quad (2.16)$$

$$[\hat{H}, \hat{S}_i^\dagger(\nu)] = \nu \hat{S}_i^\dagger(\nu). \quad (2.17)$$

By rewriting the interaction Hamiltonian in the Schrodinger picture and using the spectral decomposition of the superoperator $\hat{H}$:

$$\hat{H}_{int} = \sum_{k,\omega} e^{-i\omega t} \hat{S}_k(\omega) \otimes \hat{E}_k(t) = \sum_{k,\omega} e^{i\omega t} \hat{S}_k^\dagger(\omega) \otimes \hat{E}_k^\dagger(t). \quad (2.18)$$

Expanding the commutators of Eq. 2.14:

$$\begin{aligned} \frac{d}{dt}\hat{\rho}_S(t) &= -\frac{\alpha^2}{\hbar} \int_0^\infty ds Tr_E \{ [\hat{H}_{int}(t), [\hat{H}_{int}(s), \hat{\rho}(t)]] \}, \\ &= -\frac{\alpha^2}{\hbar} Tr \{ \int_0^\infty ds \hat{H}_{int}(t) \hat{H}_{int}(s) \hat{\rho}_S \otimes \hat{\rho}_E - \int_0^\infty \hat{H}_{int}(s) \hat{\rho}_S(t) \otimes \hat{\rho}_E(0) \hat{H}_{int}(t) - \\ &\quad - \int_0^\infty \hat{H}_{int}(t) \hat{\rho}_S(t) \otimes \hat{\rho}_E(0) - \int_0^\infty \hat{\rho}_S(t) \otimes \hat{\rho}_E(0) \hat{H}_{int}(s) \hat{H}_{int}(t) \}, \end{aligned} \quad (2.19)$$

now applying the spectral decomposition on the eigenoperators and after some algebra we end-up with the following:

$$\frac{d}{dt}\hat{\rho}_S(t) = \sum_{\omega, k, l} \left(\hat{\Gamma}_{kl}(\omega) [\hat{S}_l \hat{\rho}(t), \hat{S}_k^\dagger(\omega)] + \hat{\Gamma}_{lk}^\dagger(\omega) [\hat{S}_l(\omega), \hat{\rho}(t) \hat{S}_k^\dagger(\omega)] \right) \quad (2.20)$$

where $\hat{\Gamma}_{kl}(\omega) \equiv \int_0^\infty ds e^{i\omega s} Tr_E [\hat{E}_k^\dagger(t) \hat{E}_l(s) \hat{\rho}_E(0)]$ contains the effect of the bath. We also proceed to divide the dynamics into Hamiltonian and non-Hamiltonian by decomposing the operators $\hat{\Gamma}$:

$$\pi_{kl}(\omega) \equiv -\frac{i}{2} (\hat{\Gamma}_{kl}(\omega) - \hat{\Gamma}_{kl}^\dagger(\omega)); \quad (2.21)$$

$$\hat{\gamma} \equiv \hat{\Gamma}_{kl}(\omega) + \hat{\Gamma}_{kl}^\dagger(\omega). \quad (2.22)$$

Now we can separate the dynamics into the Hermitian and the non-Hermitian parts. By going back to the Schrodinger picture, we can write

$$\frac{d}{dt}\hat{\rho}_S(t) = -\frac{i}{\hbar} [\hat{H} + \hat{H}_{Ls}, \hat{\rho}(t)] + \sum_{\omega, k, l} \hat{\gamma}_{kl} \left(\hat{S}_l \hat{\rho}(t) \hat{S}_k^\dagger(\omega) - \frac{1}{2} \{ \hat{S}_k^\dagger \hat{S}_l(\omega), \hat{\rho}(t) \} \right), \quad (2.23)$$

where the $\hat{H}_{Ls}$ is called the *Lamb shift* which has the role to renormalize the system energy levels. The operator $\hat{\gamma}(\omega)$ can be diagonalized, the Lindblad form is the diagonal form when the operation $\hat{O} \hat{\gamma}(\omega) \hat{O}^\dagger$ is made.

So, the Lindblad form of the quantum master equation is the most general type of Markovian and time-homogeneous master equation describing the time evolution of the density operator that preserves the trace and being completely positive (both are required for physical systems) and we can write:

$$\frac{d}{dt}\hat{\rho}(t) = \hat{\mathcal{L}}(t)\hat{\rho}(t) = -\frac{i}{\hbar} [\hat{H}(t), \hat{\rho}(t)] + \sum_{\mu} \left(-\frac{1}{2} \hat{L}_{\mu}^\dagger(t) \hat{L}_{\mu}(t) \hat{\rho}(t) - \frac{1}{2} \hat{\rho}(t) \hat{L}_{\mu}^\dagger(t) \hat{L}_{\mu}(t) + \hat{L}_{\mu}(t) \hat{\rho}(t) \hat{L}_{\mu}^\dagger(t) \right) \quad (2.24)$$

The first term of the right hand side is the well-known Liouville-von Neumann equation, which describes the unitary evolution of the quantum system. The other term is referred as the dissipative part of the dynamics. The operators $\hat{L}_{\mu}$ is called the “Lindblad operators” or “jump operators”. In order to appreciate the physical significance of these operators, let us consider the following scenario:

- i) Writing the density operator in its spectral decomposition, $\hat{\rho} = \sum_i p_i(t) |i\rangle \langle i|$;
- ii) $\hat{H} = 0$.

Then we are investigating how the occupations changes solely by the dissipative part:

$$\begin{aligned}
\langle k | \hat{\rho} | k \rangle &= \sum_i p_i(t) \langle k | i \rangle \langle i | k \rangle = p_k(t), \\
\dot{p}_k(t) &= \langle k | \frac{d}{dt} \hat{\rho}(t) | k \rangle, \\
\dot{p}_k(t) &= 0 + \langle k | \left[\sum_{\mu} \left(-\frac{1}{2} \hat{L}_{\mu}^{\dagger}(t) \hat{L}_{\mu}(t) \hat{\rho}(t) - \frac{1}{2} \hat{\rho}(t) \hat{L}_{\mu}^{\dagger}(t) \hat{L}_{\mu}(t) + \hat{L}_{\mu}(t) \hat{\rho}(t) \hat{L}_{\mu}^{\dagger}(t) \right) \right] | k \rangle, \\
\dot{p}_k(t) &= \left(-\frac{1}{2} p_k(t) \right) \sum_{\mu} \left(\langle k | \hat{L}_{\mu}^{\dagger}(t) \hat{L}_{\mu}(t) | k \rangle + \langle k | \hat{L}_{\mu}^{\dagger}(t) \hat{L}_{\mu}(t) | k \rangle \right) + \sum_{\mu, i} \langle k | \hat{L}_{\mu}(t) p_i(t) | i \rangle \langle i | \hat{L}_{\mu}^{\dagger}(t) | k \rangle, \\
\dot{p}_k(t) &= -p_k(t) \sum_{\mu} \langle k | \hat{L}_{\mu}^{\dagger}(t) \hat{L}_{\mu}(t) | k \rangle + \sum_{\mu, i} \langle k | \hat{L}_{\mu}(t) | i \rangle \langle i | \hat{L}_{\mu}^{\dagger}(t) | k \rangle p_i(t), \\
\dot{p}_k(t) &= -\gamma_k p_k(t) + \sum_i \gamma_{k \leftarrow i} p_i(t), \tag{2.25}
\end{aligned}$$

where $\gamma_k \equiv \sum_{\mu} \langle k | \hat{L}_{\mu}^{\dagger}(t) \hat{L}_{\mu}(t) | k \rangle = \sum_i \sum_{\mu} | \langle i | \hat{L}_{\mu}(t) | k \rangle |^2$ and $\gamma_{k \leftarrow i} = \sum_{\mu} | \langle k | \hat{L}_{\mu}(t) | i \rangle |^2$, which represents the rate of transitions between the quantum states, and that is why the operators $\{\hat{L}_{\mu}\}$ are called “jump” operators.

We can rewrite the Eq. (2.25) as

$$\dot{p}_k(t) = -p_k(t) \sum_i \gamma_{i \leftarrow k} + \sum_i \gamma_{k \leftarrow i} p_i(t).$$

This equation is quite revealing: the first term tells us about the decay of the level k into the possible i other levels; the second term is related to the re-feeding of level k by all the other i levels. Notice that in both terms there will be $\gamma_{k \leftarrow k}$, and they cancel each other. This is physically reasonable, because there would not make sense to talk about the state of the system making a transition from level k to itself.

Let us apply the above to a case that we are going to explore later in this work: the two-level atom in contact with the vacuum. The transition rates for this example reads:

$$\gamma_{e \leftarrow g} = 0, \tag{2.26}$$

$$\gamma_{g \leftarrow e} = \text{Einstein A coefficient} = \Gamma = | \langle g | \hat{L} | e \rangle |^2 \rightarrow \hat{L} = \sqrt{\Gamma} \hat{\sigma}_-. \tag{2.27}$$

The first rate is just saying that the atom cannot make the transition from the ground state to the excited one when in contact with the vacuum; the second is saying that the rate is equal to the Einstein A coefficient that gives the rate at which spontaneous emission occurs. If the system makes a transition from $|e\rangle$ to $|g\rangle$, the operator that do this is $\hat{\sigma}_-$ hence we can imply the form of the Lindblad operator, accompanied by the square root of the rate Γ .

The master equation for the two-level system in contact with the vacuum reservoir reads:

$$\frac{d}{dt}\hat{\rho}(t) = -\frac{i}{\hbar}[\hat{H}(t), \hat{\rho}(t)] - \frac{\Gamma}{2}(\hat{\sigma}_+\hat{\sigma}_-\hat{\rho} + \hat{\rho}\hat{\sigma}_+\hat{\sigma}_-) + \Gamma\hat{\sigma}_-\hat{\rho}\hat{\sigma}_+. \quad (2.28)$$

From now on we will solve the above master equation to obtain the equations of motion for the elements of the density matrix of the two-level system interacting with the vacuum reservoir. These formulas will be used in Section 4.0.2. The Hamiltonian and the density operator for the two-level system can be written as:

$$\hat{H} = \frac{\hbar\omega_0}{2}\hat{\sigma}_z = \frac{\hbar\omega_0}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad (2.29)$$

$$\hat{\rho} = \begin{pmatrix} \rho_{ee}(t) & \rho_{eg}(t) \\ \rho_{ge}(t) & \rho_{gg}(t) \end{pmatrix}. \quad (2.30)$$

Also we are going to use the following relations to the raising and lowering operators:

$$\hat{\sigma}_+ = |e\rangle \langle g|; \quad (2.31)$$

$$\hat{\sigma}_- = |g\rangle \langle e|; \quad (2.32)$$

$$\hat{\sigma}_+\hat{\sigma}_- = |e\rangle \langle g|g\rangle \langle e| = |e\rangle \langle e| = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}. \quad (2.33)$$

Using Eqs. (2.31-33) and substituting in Eq. 2.28, we find:

$$\begin{aligned} \frac{d}{dt}\hat{\rho}(t) &= -\frac{i}{\hbar}[\hat{H}(t), \hat{\rho}(t)] - \frac{\Gamma}{2}(\hat{\sigma}_+\hat{\sigma}_-\hat{\rho} + \hat{\rho}\hat{\sigma}_+\hat{\sigma}_-) + \hat{\sigma}_-\hat{\rho}\hat{\sigma}_+ \\ &= -\frac{i}{\hbar}(\hat{H}(t)\hat{\rho}(t) - \hat{\rho}(t)\hat{H}(t)) - \frac{\Gamma}{2}(|e\rangle \langle e| \hat{\rho}(t) + \hat{\rho}(t) |e\rangle \langle e|) + |g\rangle \langle e| \hat{\rho}(t) |e\rangle \langle g|. \end{aligned} \quad (2.34)$$

Now using Eqs. (2.29-30) we can write the first term of the above equation as

$$\begin{aligned} &= -\frac{i}{\hbar} \left[\begin{pmatrix} \frac{\hbar\omega_0}{2} & 0 \\ 0 & -\frac{\hbar\omega_0}{2} \end{pmatrix} \begin{pmatrix} \rho_{ee}(t) & \rho_{eg}(t) \\ \rho_{ge}(t) & \rho_{gg}(t) \end{pmatrix} - \begin{pmatrix} \rho_{ee}(t) & \rho_{eg}(t) \\ \rho_{ge}(t) & \rho_{gg}(t) \end{pmatrix} \begin{pmatrix} \frac{\hbar\omega_0}{2} & 0 \\ 0 & -\frac{\hbar\omega_0}{2} \end{pmatrix} \right], \\ &= -\frac{i}{\hbar} \left[\begin{pmatrix} \frac{\hbar\omega_0}{2}\rho_{ee}(t) & \frac{\hbar\omega_0}{2}\rho_{eg}(t) \\ -\frac{\hbar\omega_0}{2}\rho_{ge}(t) & -\frac{\hbar\omega_0}{2}\rho_{gg}(t) \end{pmatrix} - \begin{pmatrix} \frac{\hbar\omega_0}{2}\rho_{ee}(t) & -\frac{\hbar\omega_0}{2}\rho_{eg}(t) \\ \frac{\hbar\omega_0}{2}\rho_{ge}(t) & -\frac{\hbar\omega_0}{2}\rho_{gg}(t) \end{pmatrix} \right], \\ &= \left[\begin{pmatrix} 0 & -i\omega_0\rho_{eg}(t) \\ i\omega_0\rho_{ge}(t) & 0 \end{pmatrix} \right]. \end{aligned} \quad (2.35)$$

Notice that this first term of Eq. 2.28 corresponds to the unitary part of the dynamics. Thus, it does not change the populations, since only the off-diagonal terms changes.

In the same manner, we can write the second term of Eq. 2.28 as:

$$\begin{aligned}
&= -\frac{\Gamma}{2} \left[\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} \rho_{ee}(t) & \rho_{eg}(t) \\ \rho_{ge}(t) & \rho_{gg}(t) \end{pmatrix} + \begin{pmatrix} \rho_{ee}(t) & \rho_{eg}(t) \\ \rho_{ge}(t) & \rho_{gg}(t) \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \right] \\
&= -\frac{\Gamma}{2} \left[\begin{pmatrix} \rho_{ee}(t) & \rho_{eg}(t) \\ 0 & 0 \end{pmatrix} + \begin{pmatrix} \rho_{ee}(t) & 0 \\ \rho_{ge}(t) & 0 \end{pmatrix} \right] \\
&= \left[\begin{pmatrix} -\Gamma\rho_{ee}(t) & -\frac{\Gamma}{2}\rho_{eg}(t) \\ -\frac{\Gamma}{2}\rho_{ge}(t) & 0 \end{pmatrix} \right].
\end{aligned} \tag{2.36}$$

Similarly, the third term of Eq. 2.28 reads:

$$\begin{aligned}
&= \rho_{ee}(t) |g\rangle \langle g|, \\
&= \begin{pmatrix} 0 & 0 \\ 0 & \Gamma\rho_{ee}(t) \end{pmatrix}.
\end{aligned} \tag{2.37}$$

Adding Eq. (2.35-37) together we obtain the equation of motion for the elements of the density matrix:

$$\begin{pmatrix} \dot{\rho}_{ee}(t) & \dot{\rho}_{ge}(t) \\ \dot{\rho}_{ge}(t) & \dot{\rho}_{gg}(t) \end{pmatrix} = \begin{pmatrix} -\Gamma\rho_{ee}(t) & -\rho_{eg}(t)(i\omega_0 + \frac{\Gamma}{2}) \\ \rho_{ge}(t)(i\omega_0 - \frac{\Gamma}{2}) & \Gamma\rho_{ee}(t) \end{pmatrix}. \tag{2.38}$$

From the above matrix equation we obtain the following system of equations:

$$\dot{\rho}_{ee}(t) = -\Gamma\rho_{ee}(t), \tag{2.39}$$

$$\dot{\rho}_{ge}(t) = -\rho_{eg}(t) \left(i\omega_0 + \frac{\Gamma}{2} \right), \tag{2.40}$$

$$\dot{\rho}_{ge}(t) = \rho_{ge}(t) \left(i\omega_0 - \frac{\Gamma}{2} \right), \tag{2.41}$$

$$\dot{\rho}_{gg}(t) = \Gamma\rho_{ee}(t). \tag{2.42}$$

By solving the above system of equations we obtain the following solutions:

$$\frac{d\rho_{ee}(t)}{\rho_{ee}} = -\Gamma dt \rightarrow \rho_{ee}(t) = \rho_{ee}(0)e^{-\Gamma t}; \tag{2.43}$$

$$\frac{d\rho_{eg}}{\rho_{eg}} = \left(-i\omega_0 - \frac{\Gamma}{2} \right) dt \rightarrow \rho_{eg}(t) = \rho_{eg}(0)e^{(-i\omega_0 - \frac{\Gamma}{2})t} = \rho_{ge}^*(t); \tag{2.44}$$

$$\rho_{gg}(t) + \rho_{ee}(t) = 1 \rightarrow \rho_{gg}(t) = 1 - \rho_{ee}(0)e^{-\Gamma t}. \tag{2.45}$$

These equations of motion are going to be used later. They describe, considering the Markov approximation and weak interaction, how the two level atom evolves in time when in contact with a zero temperature bath (vacuum).

2.3 Density operator

The density operator allows one describe the theory of measurements in general ensembles, pure or mixed. It is, one may not have complete information about the system that is being subjected to a measurement. As in classical mechanics, one employ a concept of a *density function* in the phase space. Under quantization, we have the density operator, which carries information about the occupation probability of each possible ket that compose the ensemble. Therefore enabling one to calculate the expectation values, over a general ensemble, of quantum mechanical observables where both the quantum and statistical expectation values are considered.

The density operator is defined as (23):

$$\rho \equiv \sum_i w_i |\alpha^i\rangle \langle \alpha^i|, \quad (2.46)$$

where w_i are the probabilities weights of finding the states $|\alpha^i\rangle$ of the ensemble. The number of states (i) may exceed the dimensionality of the Hilbert space, thus $\{|\alpha^i\rangle\}$ does not form a complete orthonormal basis.

One could also write the density operator in its spectral decomposition, once ρ is an Hermitian operator:

$$\rho_A(t) = \sum_i p_i(t) |\psi_i(t)\rangle \langle \psi_i(t)|, \quad (2.47)$$

where $p_i(t)$ refers to the instantaneous probability occupation of the instantaneous eigenkets $|\psi_i(t)\rangle$.

3 Proposal for “refined” or “unambiguous” heat and work definitions in quantum thermodynamics

When two thermodynamic systems interact they exchange energy until all the fluxes ceases and new equilibrium states are reached. To address precisely which portion of that energy exchanged is of the form of heat or work turns out to be a non-trivial problem when we are dealing with systems as quantum ensembles.

The proposal for heat and work definitions in quantum thermodynamics that we are going to present and further investigate are found in the papers by Ahmadi et al. (18) and, independently, Alipour et al. (19). The core physical reasoning for these definitions are due to Clausius: *heat* is defined as the energy in transit which is associated with an entropy change of the system and *work* is the energy exchanged that does not cause any change in the entropy.

First of all let us consider the classical apparatus showed in figure 1: A and B are classical gases, the total system $A + B$ is enclosed by some rigid and adiabatic wall; the wall that separates A and B are made diathermal and movable so they can exchange both heat and work. If we choose to look at system A, all the possible energy transfers can be summarized as:

$$\begin{aligned} dW_A &= dW_{A,external} + dW_{A,exchanged}, \\ dQ_A &= dQ_{A,exchanged} \end{aligned}$$

as the work is mechanical, it is related to the volume variation of the system. So in classical setups it is trivial to distinguish heat from the work by employing some kind of walls. But for quantum setups its not that trivial. The fundamental question then arises: how can one come up with some unambiguously definitions of heat and work in quantum regime?

Examining the internal energy of a quantum statistical system and how it changes in time,

$$\begin{aligned} E_A(t) &= \langle H_A(t) \rangle \equiv \text{Tr} \{ \rho_A(t) H_A(t) \} \\ dE_A(t) &= \text{Tr} \{ d[\rho_A(t) H_A(t)] \} \\ dE_A(t) &= \text{Tr} \{ d\rho_A(t) H_A(t) \} + \text{Tr} \{ \rho_A(t) dH_A(t) \} \end{aligned} \tag{3.1}$$

notice that the above formula is actually the first law of thermodynamics but stated for a quantum statistical system in the formalism by von Neumann (1). It is somehow intuitive

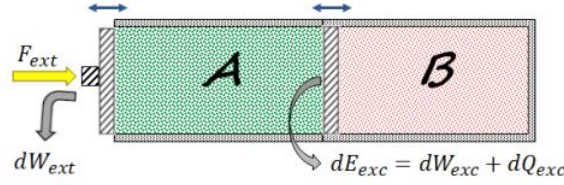


Figura 1 – A and B are classical gases. They are set apart by a movable and diathermal wall, hence they can exchange energy in the form of heat and work. Figure from (18).

to associate the variation of the local Hamiltonian as having something to do with work, once it represents an external change (it can be manipulated); and a variation on the system (populations) as related to heat as can be seen in Alicki’s definitions:

$$\begin{aligned} d \langle Q_A(t) \rangle &\equiv \text{Tr}[d\rho_A(t)H_A(t)], \\ d \langle W_A(t) \rangle &\equiv \text{Tr}[\rho_A(t)dH_A(t)]. \end{aligned}$$

Notice that according to the above definitions, the work is related only to the external contribution. Taking the hypothesis of the existence of some other source of work transfer being true, i.e. energy as work being transferred via the interaction, how could one describe this energy?

As mentioned before, the approach taken by Ahmadi et al. and Alipour et al. is that the variation in entropy is associated with heat, while work is not. To this end, it is worth to take a look at the entropy of these systems. An important fact that has to be made clear is that for all that matters, one is taking as the thermodynamical entropy the von Neumann’s entropy,

$$S(\rho_A(t)) \equiv -\text{Tr}[\rho_A(t) \ln \rho_A(t)]. \quad (3.2)$$

One can decompose the density matrix in its diagonal form, once ρ is an Hermitian operator:

$$\rho_A(t) = \sum_i^d p_i(t) |\psi_i(t)\rangle \langle \psi_i(t)|, \quad (3.3)$$

so, the entropy of a system defined by ρ can be written as:

$$\begin{aligned} S(\rho_A(t)) &= -\sum_i^d \langle \psi_i(t) | \rho_A(t) \ln \rho_A(t) | \psi_i(t) \rangle, \\ S(\rho_A(t)) &= -\sum_i^d p_i(t) \ln p_i(t). \end{aligned} \quad (3.4)$$

By differentiating the above equation we find:

$$\begin{aligned}
dS(\rho_A(t)) &= d \left[- \sum_i^d p_i(t) \ln p_i(t) \right], \\
&= - \sum_i^d d [p_i(t) \ln p_i(t)], \\
&= - \sum_i^d [dp_i(t) \ln p_i(t) + p_i(t) dp_i(t)], \\
&= - \sum_i^d dp_i(t) \ln p_i(t) - d \sum_i^d p_i(t), \\
&= - \sum_i^d dp_i(t) \ln p_i(t).
\end{aligned}$$

Notice that the variation of the entropy is related to the change in the occupation probabilities of the states that compose the ensemble.

So far we know that the heat expression should come with a term $dp_i(t)$. Let us just look at how the system evolves in time (using $\rho_A(t) = \sum_i^d p_i(t) |\psi_i(t)\rangle \langle \psi_i(t)|$):

$$\begin{aligned}
d\rho_A(t) &= \sum_i^d d [p_i(t) |\psi_i(t)\rangle \langle \psi_i(t)|], \\
&= \sum_i^d [dp_i(t) |\psi_i(t)\rangle \langle \psi_i(t)| + p_i(t) d(|\psi_i(t)\rangle \langle \psi_i(t)|)], \\
&= \sum_i^d dp_i(t) |\psi_i(t)\rangle \langle \psi_i(t)| + \sum_i^d p_i(t) d(|\psi_i(t)\rangle \langle \psi_i(t)|). \tag{3.5}
\end{aligned}$$

The first term on the right hand side (rhs) of the above equation has the term $dp_i(t)$ which is related to the non-unitary part of the evolution; the second term is the unitary part of the evolution, therefore it is not associated with any entropy change.

To couple the above result with the first law they simply used Eq.(3.5) in the first term of the rhs of eq.(3.1):

$$\begin{aligned}
dE_A(t) &= \text{Tr}\{d\rho_A(t)H_A(t)\} + \text{Tr}\{\rho_A(t)dH_A(t)\}, \\
&= \text{Tr} \left\{ \left[\sum_i^d dp_i(t) |\psi_i(t)\rangle \langle \psi_i(t)| + \sum_i^d p_i(t) d(|\psi_i(t)\rangle \langle \psi_i(t)|) \right] H_A(t) + \rho_A(t) dH_A(t) \right\}, \\
&= \text{Tr} \left\{ \sum_i^d dp_i(t) |\psi_i(t)\rangle \langle \psi_i(t)| H_A(t) \right\} + \text{Tr} \left\{ \sum_i^d p_i(t) d(|\psi_i(t)\rangle \langle \psi_i(t)|) H_A(t) \right\} + \text{Tr} \{ \rho_A dH_A(t) \}.
\end{aligned}$$

Therefore they ended-up with the following definitions:

$$dQ_{A,exchanged} \equiv \text{Tr} \left\{ \sum_i^d dp_i(t) |\psi_i(t)\rangle \langle \psi_i(t)| H_A(t) \right\}, \tag{3.6}$$

$$dW_{A,exchanged} \equiv \text{Tr} \left\{ \sum_i^d p_i(t) d(|\psi_i(t)\rangle \langle \psi_i(t)|) H_A(t) \right\}, \tag{3.7}$$

$$dW_{A,external} \equiv \text{Tr} \{ \rho_A dH_A(t) \}. \tag{3.8}$$

The term of exchanged work can be written in a more insightful way, by noticing that:

$$\begin{aligned} d(|\psi_i(t)\rangle \langle \psi_i(t)|) &= |\psi_i(t+dt)\rangle \langle \psi_i(t+dt)| - |\psi_i(t)\rangle \langle \psi_i(t)|, \\ &= U(dt) |\psi_i(t)\rangle \langle \psi_i(t)| U^\dagger(dt) - |\psi_i(t)\rangle \langle \psi_i(t)|. \end{aligned}$$

Hence,

$$\begin{aligned} \sum_i^d p_i(t) d(|\psi_i(t)\rangle \langle \psi_i(t)|) H_A &= \sum_i^d p_i(t) [U(dt) |\psi_i(t)\rangle \langle \psi_i(t)| U^\dagger(dt) - |\psi_i(t)\rangle \langle \psi_i(t)|] H_A, \\ &= [U(dt) \rho_A(t) U^\dagger(dt) - \rho_A(t)] H_A \equiv d\rho_A^U H_A. \end{aligned}$$

Using the above results, we can rewrite Eq. (3.7) as

$$dW_{A,exchanged} = \text{Tr} \left\{ \sum_i^d p_i(t) d(|\psi_i(t)\rangle \langle \psi_i(t)|) H_A(t) \right\} = \text{Tr} \left\{ d\rho_A^U(t) H_A(t) \right\},$$

which shows that this portion of the work is only related to the unitary evolution of the system density operator.

The formulas (3.6-8) are the ones that we are going to use in the next chapter to study the energy exchange between quantum systems while they interact. The authors claim that these new formulas defines unambiguously heat and work in the quantum thermodynamical context. This statement is exactly what we are going to investigate in chapter 4.

4 Results and Discussions

We want to analyse two problems that the open quantum system theory covers: the dephasing interaction between two qubits and the two level atom in contact with the vacuum reservoir. We are interested in applying the formal definitions of heat and work that we presented in the last chapter (3) to one of the subsystems as the global system evolves in time. Our main goal is to understand and investigate the implications of these definitions, contrasting with first principles of Thermodynamics and Statistical Quantum Mechanics.

4.0.1 Two Qubits dephasing interaction

We are dealing with a two qbits system interacting according to the following Hamiltonian:

$$H_{int} = \hbar\chi\sigma_z^A \otimes \sigma_z^B,$$

where χ is the strength of the interaction. For simplicity, in the following we will consider $\chi = 1$ and $\hbar = 1$. For the system A and B we have:

$$H_A = \frac{\omega_0}{2}\sigma_z^A, H_B = \frac{\omega_0}{2}\sigma_z^B.$$

We are going to investigate the initial states:

$$\rho_A(0) = \begin{pmatrix} p & c \\ \bar{c} & 1-p \end{pmatrix}; \rho_B(0) = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}.$$

Using:

$$|+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}; |-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix},$$

we can also write the initial states in the form:

$$\rho_A(0) = p|+\rangle_A \langle +| + c|+\rangle_A \langle -| + \bar{c}|-\rangle_A \langle +| + (1-p)|-\rangle_A \langle -|; \quad (4.1)$$

$$\rho_B(0) = \frac{1}{2}|+\rangle_B \langle +| + 0|+\rangle_B \langle -| + 0|-\rangle_B \langle +| + \frac{1}{2}|-\rangle_B \langle -|. \quad (4.2)$$

Hence, the composite system is given by the tensor product:

$$\rho_{AB}(0) = \rho_A(0) \otimes \rho_B(0), \quad (4.3)$$

$$\begin{aligned} &= \frac{p}{2} |+\rangle_A \langle +| \otimes |+\rangle_B \langle +| + \frac{p}{2} |+\rangle_A \langle +| \otimes |-\rangle_B \langle -| + \\ &+ \frac{c}{2} |+\rangle_A \langle -| \otimes |+\rangle_B \langle +| + \frac{c}{2} |+\rangle_A \langle -| \otimes |-\rangle_B \langle -| + \\ &+ \frac{\bar{c}}{2} |-\rangle_A \langle +| \otimes |+\rangle_B \langle +| + \frac{\bar{c}}{2} |-\rangle_A \langle +| \otimes |-\rangle_B \langle -| + \\ &+ \frac{(1-p)}{2} |-\rangle_A \langle -| \otimes |+\rangle_B \langle +| + \frac{(1-p)}{2} |-\rangle_A \langle -| \otimes |-\rangle_B \langle -|, \\ \rho_{AB}(0) &= \frac{p}{2} |++\rangle \langle ++| + \frac{p}{2} |+-\rangle \langle +-| + \frac{(1-p)}{2} |-+\rangle \langle -+| + \frac{(1-p)}{2} |--\rangle \langle --| + \\ &+ \frac{c}{2} |++\rangle \langle -+| + \frac{c}{2} |+-\rangle \langle --| + \frac{\bar{c}}{2} |-+\rangle \langle ++| + \frac{\bar{c}}{2} |--\rangle \langle +-|. \end{aligned} \quad (4.4)$$

Notice that we shortened the notation for the tensor product: the first and second entry refers to the kets belonging to the Hilbert space of system A and B, respectively ($|+\rangle_A \otimes |+\rangle_B = |++\rangle$).

The total evolution is unitary, all Hamiltonians are time independent and they commute. We can write the global time evolution operator as follows:

$$\begin{aligned} \mathcal{U} &= e^{-iH_A t} e^{-iH_B t} e^{-iH_{int} t}, \\ \mathcal{U} &= e^{-i\frac{\omega_0}{2}\sigma_z^A} e^{-i\frac{\omega_0}{2}\sigma_z^B} e^{-i\sigma_z^A \otimes \sigma_z^B t}, \end{aligned} \quad (4.5)$$

and

$$\mathcal{U}^\dagger = e^{+i\frac{\omega_0}{2}\sigma_z^A} e^{+i\frac{\omega_0}{2}\sigma_z^B} e^{+i\sigma_z^A \otimes \sigma_z^B t}. \quad (4.6)$$

For the time evolution of the composed density operator:

$$\rho_{AB}(t) = \mathcal{U} \rho_{AB}(0) \mathcal{U}^\dagger \quad (4.7)$$

plugging Eq. 4.4 in the the above expression and using:

- i) $e^{(\sigma_z)} |+\rangle = e^1 |+\rangle$;
- ii) $e^{(\sigma_z)} |-\rangle = e^{-1} |-\rangle$;

one would eventually end-up with the following density matrix:

$$\rho_{AB}(t) = \begin{pmatrix} \frac{p}{2} & 0 & \frac{c}{2} e^{-i\omega_0 t} e^{-2it} & 0 \\ 0 & \frac{p}{2} & 0 & \frac{c}{2} e^{-i\omega_0 t} e^{2it} \\ \frac{\bar{c}}{2} e^{i\omega_0 t} e^{2it} & 0 & \frac{(1-p)}{2} & 0 \\ 0 & \frac{\bar{c}}{2} e^{i\omega_0 t} e^{-2it} & 0 & \frac{(1-p)}{2} \end{pmatrix},$$

notice that the sum over the diagonal terms equals to one, as should be.

Now, we are going to apply the formalism that we presented in section 3. Let us look to the system A, i.e. tracing over the degrees of freedom of system B:

$$\rho_A(t) = \text{Tr}_B \{ \rho_{AB}(t) \}. \quad (4.8)$$

Computing the trace over each member of the system B:

$$\begin{aligned}
Tr_B\{|++\rangle\langle++|\} &= |+\rangle_A\langle+|; \\
Tr_B\{|++\rangle\langle+-|\} &= 0; \\
Tr_B\{|++\rangle\langle-+|\} &= |+\rangle_A\langle-|; \\
Tr_B\{|++\rangle\langle--|\} &= 0; \\
Tr_B\{|+-\rangle\langle++|\} &= 0; \\
Tr_B\{|+-\rangle\langle+-|\} &= |+\rangle_A\langle+|; \\
Tr_B\{|+-\rangle\langle-+|\} &= 0; \\
Tr_B\{|+-\rangle\langle--|\} &= |+\rangle_A\langle-|; \\
Tr_B\{|-+\rangle\langle++|\} &= |-\rangle_A\langle+|; \\
Tr_B\{|-+\rangle\langle+-|\} &= 0; \\
Tr_B\{|-+\rangle\langle-+|\} &= |-\rangle_A\langle-|; \\
Tr_B\{|-+\rangle\langle--|\} &= 0; \\
Tr_B\{|--\rangle\langle++|\} &= 0; \\
Tr_B\{|--\rangle\langle+-|\} &= |-\rangle_A\langle+|; \\
Tr_B\{|--\rangle\langle-+|\} &= 0; \\
Tr_B\{|--\rangle\langle--|\} &= |-\rangle_A\langle-|.
\end{aligned}$$

Therefore,

$$\begin{aligned}
\rho_A(t) &= \frac{p}{2} |+\rangle_A\langle+| + \frac{c}{2} e^{-i\omega_0 t} e^{-2it} |+\rangle_A\langle-| + \frac{p}{2} |+\rangle_A\langle-| + \\
&\quad + \frac{c}{2} e^{-i\omega_0 t} e^{2it} |+\rangle_A\langle-| + \frac{\bar{c}}{2} e^{i\omega_0 t} e^{2it} |-\rangle_A\langle+| + \\
&\quad + \frac{(1-p)}{2} |-\rangle_A\langle-| + \frac{\bar{c}}{2} e^{i\omega_0 t} e^{-2it} |-\rangle_A\langle+| + \frac{(1-p)}{2} |-\rangle_A\langle-|; \\
\rho_A(t) &= p |+\rangle\langle+| + \frac{c}{2} e^{-i\omega_0 t} (e^{-2it} + e^{+2it}) |+\rangle\langle-| + \\
&\quad + \frac{\bar{c}}{2} e^{i\omega_0 t} (e^{+2it} + e^{-2it}) |-\rangle\langle+| + (1-p) |-\rangle\langle-|.
\end{aligned}$$

Notice that the terms in parenthesis can be recast as $2 \cos 2t = e^{i2t} + e^{-i2t}$ with $\hbar = 1$; applying this and rewriting $\rho_A(t)$ in the interaction picture,

$$\begin{aligned}
\rho_{A,int}(t) &= e^{+i\frac{\omega_0}{2}\sigma_z^A} [p |+\rangle\langle+| + c \cos 2t e^{-i\omega_0 t} |+\rangle\langle-| + \\
&\quad + \bar{c} \cos 2t e^{i\omega_0 t} |-\rangle\langle+| + (1-p) |-\rangle\langle-|] e^{-i\frac{\omega_0}{2}\sigma_z^A};
\end{aligned} \tag{4.9}$$

$$\rho_{A,int}(t) = p |+\rangle\langle+| + c \cos 2t |+\rangle\langle-| + \bar{c} \cos 2t |-\rangle\langle+| + (1-p) |-\rangle\langle-|, \tag{4.10}$$

in the matrix form:

$$\rho_A(t) = \begin{pmatrix} p & c \cos 2t \\ \bar{c} \cos 2t & 1-p \end{pmatrix}. \tag{4.11}$$

Notice that the internal energy of the subsystem A is invariant during the dynamics:

$$E_0 = \text{Tr}\{\rho_A(0)H_A\} = \frac{\omega_0}{2}(2p-1); \quad (4.12)$$

$$E_t = \text{Tr}\{\rho_A(t)H_A\} = \frac{\omega_0}{2}(2p-1); \quad (4.13)$$

$$\rightarrow \Delta E = 0. \quad (4.14)$$

If we apply the standard formalism, i.e. Eqs. (1.2,1.3), as the Hamiltonian H_A does not depend on time, we get $dW_A = 0$. Hence, the first law of thermodynamics:

$$\Delta E = \int_0^t dQ_A(t') + \int_0^t dW_A(t'), \quad (4.15)$$

$$0 = \int_0^t dQ_A(t') + 0 \quad (4.16)$$

$$\rightarrow dQ_A = 0. \quad (4.17)$$

As pointed out in reference (18), the above result is an inconsistency of the standard formulation: the system is interacting and neither work nor heat is being exchanged. As we should have guessed, once the Alicki's formulation was developed to describe a system in contact with a reservoir, taken as having infinite degrees of freedom.

Let us examine what we get by applying the new set of definitions (3.6,3.7,3.8). In order to do it, we proceed to diagonalize the matrix $\rho_A(t)$, Eq. (4.11). The expression for the instantaneous eigenvalues have the form

$$p_1(t) = \frac{1}{2} + \frac{\sqrt{1 + 4c^2 \cos 2t^2 + 4p^2 - 4p}}{2}, \quad (4.18)$$

$$p_2(t) = \frac{1}{2} - \frac{\sqrt{1 + 4c^2 \cos 2t^2 + 4p^2 - 4p}}{2}, \quad (4.19)$$

and the (unnormalized) eigenstates read

$$|\psi_1(t)\rangle = \begin{pmatrix} \frac{2c \cos 2t}{1 + \sqrt{4c^2 \cos 2t^2 + 4(p - \frac{1}{2})^2 - 2p}} \\ 1 \end{pmatrix}, \quad (4.20)$$

$$|\psi_2(t)\rangle = \begin{pmatrix} \frac{-2c \cos 2t}{-1 + \sqrt{4c^2 \cos 2t^2 + 4(p - \frac{1}{2})^2 + 2p}} \\ 1 \end{pmatrix}. \quad (4.21)$$

Using the new proposed equations for heat and work that was presented in Chapter 3:

$$\frac{d}{dt} \langle Q_A \rangle = \sum_{i=1}^2 \frac{dp_i(t)}{dt} \langle \psi_i(t) | H_A(t) | \psi_i(t) \rangle; \quad (4.22)$$

$$\frac{d}{dt} \langle dW_A \rangle = \sum_{i=1}^2 p_i(t) \frac{d}{dt} [\langle \psi_i(t) | H_A(t) | \psi_i(t) \rangle]. \quad (4.23)$$

Using Eqs. (4.18-19) and the normalized version of Eqs. (4.20-21), we can rewrite Eqs. (4.21 and 4.22) as:

$$\frac{d}{dt} \langle Q_A \rangle = - \frac{8 \left(p - \frac{1}{2}\right) \sin 2tc^2 \cos 2t\omega_0}{4c^2 \cos 2t^2 + 4 \left(p - \frac{1}{2}\right)^2}; \quad (4.24)$$

$$\frac{d}{dt} \langle dW_A \rangle = \frac{8 \left(p - \frac{1}{2}\right) \sin 2tc^2 \cos 2t\omega_0}{4c^2 \cos 2t^2 + 4 \left(p - \frac{1}{2}\right)^2}. \quad (4.25)$$

Notice from Eq. (4.24,4.25) that $dQ_A = -dW_A$, and therefore the first law is satisfied. Thus, in some cases the standard formalism can not differentiate the energy exchanged in the form of work, but apparently the new set can.

We can ask if this result is general or not. Let us investigate the following specific case using $p = \frac{1}{2}$ and $c = \bar{c} = \frac{1}{2}$:

$$\rho_A(t) = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \cos 2t \\ \frac{1}{2} \cos 2t & \frac{1}{2} \end{pmatrix}.$$

Our goal now is to diagonalize this matrix in order to obtain its eigenvalues and eigenvectors. Thus,

$$\det\{(\rho_A(t) - \lambda \mathbb{1})\} = 0,$$

$$\lambda^2 - \lambda + \frac{1}{4} (1 - \cos^2 2t) = 0.$$

This is a typical second order equation with solutions:

$$\lambda_1(t) = p_1(t) = \frac{1 - \cos 2t}{2} = \sin^2 t, \quad (4.26)$$

$$\lambda_2(t) = p_2(t) = \frac{1 + \cos 2t}{2} = \cos^2 t, \quad (4.27)$$

where we identified $\lambda_i(t) = p_i(t)$ for $i = 1, 2$; $p_i(t)$ are the eigenvalues of the density operator that represents the system A evolved in time.

Now for the eigenvectors

$$\begin{pmatrix} \frac{1}{2} & \frac{1}{2} \cos 2t \\ \frac{1}{2} \cos 2t & \frac{1}{2} \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \sin^2 t \begin{pmatrix} x \\ y \end{pmatrix}, \quad (4.28)$$

which leads us to the following system of equations:

$$\frac{x}{2} + \frac{y \cos 2t}{2} = x \sin^2 t \quad (4.29)$$

$$\frac{x \cos 2t}{2} + \frac{y}{2} = y \sin^2 t. \quad (4.30)$$

Working with Eqs. (4.28, 4.29),

$$\begin{aligned} x \left(\frac{1}{2} - \sin^2 t \right) &= -\frac{y \cos 2t}{2} \\ x &= -\frac{\cos 2t}{2} \frac{2y}{(1 - 2 \sin^2 t)} \\ x &= -y. \end{aligned} \quad (4.31)$$

Hence choosing $x = 1$ we get $y = -1$ and we can write the first eigenvector as

$$|\psi_1\rangle = \frac{1}{\sqrt{2}} [|0\rangle - |1\rangle]. \quad (4.32)$$

For the second eigenvector we follow the same procedure and write:

$$\begin{pmatrix} \frac{1}{2} & \frac{1}{2} \cos 2t \\ \frac{1}{2} \cos 2t & \frac{1}{2} \end{pmatrix} \begin{pmatrix} x' \\ y' \end{pmatrix} = \cos^2 t \begin{pmatrix} x' \\ y' \end{pmatrix}, \quad (4.33)$$

from which we can write the following system of equations:

$$\frac{x'}{2} + \frac{y' \cos 2t}{2} = x' \cos^2 t, \quad (4.34)$$

$$\frac{x' \cos^2 2t}{2} + \frac{y'}{2} = y' \cos^2 t. \quad (4.35)$$

Solving the above system of equations we obtain:

$$\begin{aligned} x' \left(\frac{1}{2} - \cos^2 t \right) &= -\frac{y' \cos 2t}{2}, \\ x' &= -\frac{\cos 2t}{2} \frac{2y'}{(1 - 2 \cos^2 t)}, \\ x' &= y', \end{aligned} \quad (4.36)$$

allowing us to write to the second eigenvector:

$$|\psi_2\rangle = \frac{1}{\sqrt{2}} [|0\rangle + |1\rangle]. \quad (4.37)$$

Note that these states are orthonormal, i.e. $\langle \psi_i | \psi_j \rangle = \delta_{i,j}$.

We can now rewrite the density operator for the system A in its diagonal form:

$$\begin{aligned} \rho_A(t) &= \sum_{i=1}^2 p_i |\psi_i\rangle \langle \psi_i|, \\ \rho_A(t) &= \sin^2 t |\psi_1\rangle \langle \psi_1| + \cos^2 t |\psi_2\rangle \langle \psi_2|. \end{aligned}$$

Recalling 4.22:

$$\frac{d}{dt} \langle Q_A \rangle = \sum_{i=1}^2 \frac{dp_i(t)}{dt} \langle \psi_i(t) | H_A(t) | \psi_i(t) \rangle \quad (4.38)$$

$$\frac{d}{dt} \langle Q_A \rangle = \frac{dp_1(t)}{dt} \langle \psi_1(t) | \frac{\omega_0 \sigma_z^A}{2} | \psi_1(t) \rangle + \frac{dp_2(t)}{dt} \langle \psi_2(t) | \frac{\omega_0 \sigma_z^A}{2} | \psi_2(t) \rangle. \quad (4.39)$$

The above equations for the heat can be written as

$$\frac{d}{dt} \langle Q_A \rangle = \frac{dp_1(t)}{dt} \frac{\omega_0}{2} \langle \psi_1(t) | \psi_2(t) \rangle + \frac{dp_2(t)}{dt} \frac{\omega_0}{2} \langle \psi_2(t) | \psi_1(t) \rangle = 0,$$

Where we have used:

$$\sigma_z |\psi_1\rangle = |\psi_2\rangle, \quad (4.40)$$

$$\sigma_z |\psi_2\rangle = |\psi_1\rangle, \quad (4.41)$$

$$\langle \psi_1 | \psi_2 \rangle = 0. \quad (4.42)$$

Now for the external work:

$$\frac{d}{dt} \langle W_{A(ext)} \rangle = \text{Tr} \left\{ \rho_A \frac{d}{dt} H_A(t) \right\} = 0,$$

since H_A does not depend on time.

For the exchanged work, we use Eq. (4.23):

$$\frac{d}{dt} \langle W_{A(exc)} \rangle = \text{Tr} \left\{ \sum_i^d p_i(t) \frac{d}{dt} (|\psi_i(t)\rangle \langle \psi_i(t)|) H_A(t) \right\} = 0,$$

because $(|\psi_i\rangle \langle \psi_i|)$ also does not depend on time.

In this specific example we spotted the same lack in satisfying the first law that we witnessed before with the standard formalism. Therefore, the same criticism also applies for this new formalism when dealing with only two systems interacting. This seems to suggest that this new proposal is not general as the authors claim.

In the next section we are going to use the Markov Master Equation formalism that we presented in 2.2 to deal with the problem of a two level system in contact with a zero temperature bath, also called “vacuum”. We are going to show that these new formulas can lead to some unusual behaviors with regards to the energy exchanged between the two systems.

4.0.2 Two level atom in contact with a heat bath at zero temperature

The system that we are dealing with consists of a two level atom interacting with a thermal reservoir. The total Hamiltonian of the problem is

$$H = H_S + H_B + H_{SB},$$

$$H = \frac{\hbar\omega_0}{2} \sigma_z + \sum_i \hbar\omega_i a^\dagger(\omega_i) a(\omega_i) + \sum_i g(\omega_i) (\sigma_- a(\omega_i)^\dagger + \sigma_+ a(\omega_i)).$$

The dynamics is memoryless and the coupling between the system and the environment is weak. The equations of motion for the state of the system in contact with the vacuum were deduced Eqs. (2.43,2.44,2.45):

$$\begin{aligned}\rho_{ee}(t) &= \rho_{ee}(0)e^{-\Gamma t}, \\ \rho_{eg}(t) &= \rho_{ge}(t) = \rho_{eg}(0)e^{-\frac{1}{2}\Gamma t}, \\ \rho_{gg}(t) &= 1 - \rho_{ee}(0)e^{-\Gamma t}.\end{aligned}$$

Where Γ is the Einstein A coefficient for spontaneous emission that represents the decay of the atomic excited levels; notice that we absorbed the global phase that appeared in Eq. (2.44), once its a global phase and won't affect our description.

In general we can construct the following time dependent density operator for the system of interest with the aid of the above solutions of the master equation,

$$\rho(t) = \begin{pmatrix} \rho_{ee}(0)e^{-\Gamma t} & \rho_{eg}(0)e^{-\frac{1}{2}\Gamma t} \\ \rho_{eg}(0)e^{-\frac{1}{2}\Gamma t} & 1 - \rho_{ee}(0)e^{-\Gamma t} \end{pmatrix}.$$

By the diagonalization process of a two by two matrix one gets the following time dependent expression for the eigenvalues, the instantaneous populations:

$$p_1(t) = \left(\frac{1 + \sqrt{4\rho_{ee}^2 + 4\rho_{eg}^2 - 4\rho_{ee} + 1}}{2} \right); \quad (4.43)$$

$$p_2(t) = \left(\frac{1 - \sqrt{4\rho_{ee}^2 + 4\rho_{eg}^2 - 4\rho_{ee} + 1}}{2} \right). \quad (4.44)$$

and for the instantaneous (unnormalized) eigenkets:

$$|\psi_1(t)\rangle = \begin{pmatrix} -\frac{\rho_{eg}}{-\frac{1}{2} - \frac{\sqrt{4\rho_{ee}^2 + 4\rho_{eg}^2 - 4\rho_{ee} + 1}}{2} + \rho_{ee}} \\ 1 \end{pmatrix}; \quad (4.45)$$

$$|\psi_2(t)\rangle = \begin{pmatrix} -\frac{\rho_{eg}}{-\frac{1}{2} + \frac{\sqrt{4\rho_{ee}^2 + 4\rho_{eg}^2 - 4\rho_{ee} + 1}}{2} + \rho_{ee}} \\ 1 \end{pmatrix}; \quad (4.46)$$

Now we use the definitions of heat and work fluxes Eqs. (4.22,4.23)

$$\begin{aligned}\frac{d}{dt} \langle Q_S \rangle &= \sum_{i=1}^2 \frac{d}{dt} (p_i(t)) \langle \psi_i(t) | H_S | \psi_i(t) \rangle, \\ \frac{d}{dt} \langle W_S \rangle &= \sum_{i=1}^2 p_i(t) \frac{d}{dt} (\langle \psi_i(t) | H_S | \psi_i(t) \rangle),\end{aligned}$$

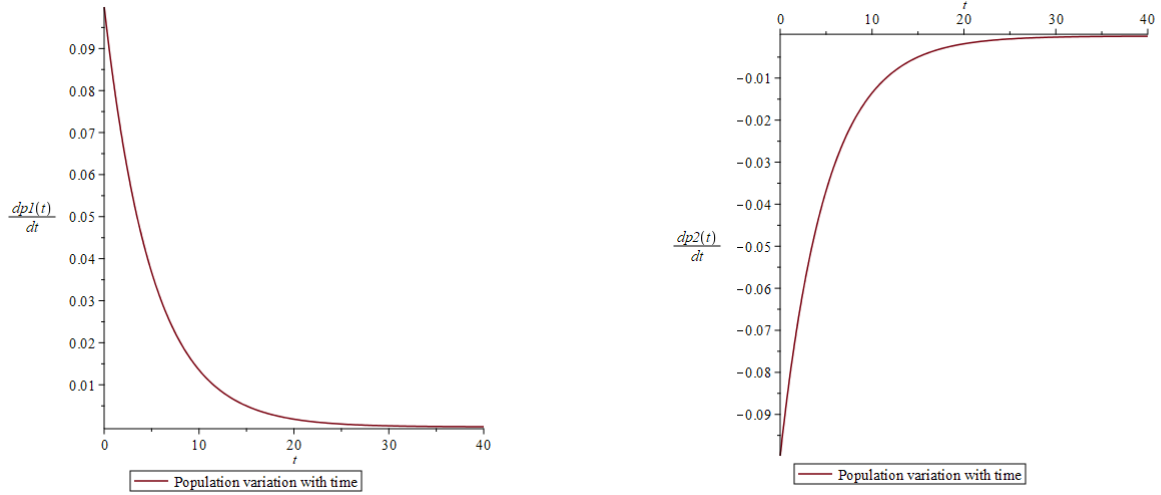


Figure 2 – Population variations with time. On the left we have the variation of $p_1(t)$. Notice that these variations are negligible.

for the case where the initial state is the following unpolarized beam (incoherent mixture):

$$\rho(0) = \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}.$$

In the following numerical calculations we use $\Gamma = 0.2s^{-1}$. As can be seen in figure 2, the variations on the populations $p_1(t)$ and $p_2(t)$ are very small hence justifying the “noisy” aspect of the heat flux in figure 3. The system has no coherence, which means that the state won’t change in time, i.e. it doesn’t show any instantaneous eigenkets, therefore the work flux is also zero. Notice that, effectively, the heat and the work fluxes are zero for this state.

It happens because this ensemble has no coherence. In fact we can generalize that for any incoherent state there will be no work whatsoever, once the expressions (4.45,4.46) depends on the off-diagonal element of the density matrix. Thus there is no information, hence energy, being exchanged about the phase relation of the members of the ensemble.

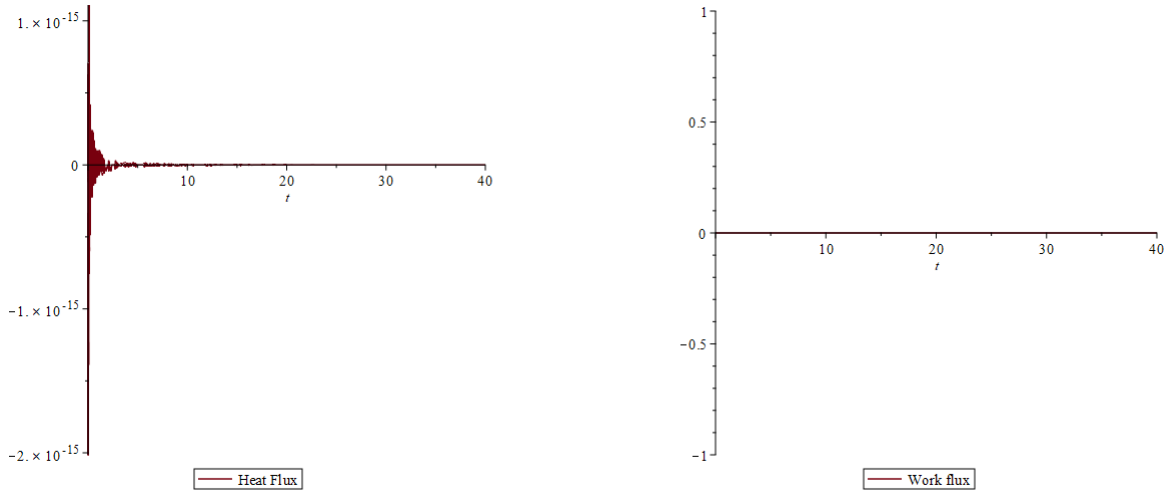


Figura 3 – Heat and work fluxes *versus* time for the incoherent mixture in contact with the vacuum. The heat flux presents a negligible fluctuation and the work flux is exactly zero, it happens because the states are not changing with time.

Now if we take initially the coherent mixed state, which is a linear superposition of the kets in the computational basis,

$$\rho(0) = \begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix}.$$

In order to understand this ensemble is worthwhile to take a look at the formulas for the eigenprobabilities, Eqs. 4.43 and 4.44. At time $t = 0$, $p_1(0) = 1$ and $p_2(0) = 0$, it means that, initially, the ensemble can be exactly characterized by $|\psi_1(0)\rangle = \frac{1}{\sqrt{2}}(|+\rangle + |-\rangle)$, which can be seen by the normalized version of Eqs. (4.45, 4.46) at $t = 0$. In figure 4, we plotted a graph that tracks how the eigenprobabilities given by Eqs. (4.43,4.44) change in time. The behavior for the heat flux and the total heat for the system are presented in figure 5; the work and work flux is presented in fig. 6.

From Figure 4, we can observe that the eigenprobabilities $p_1(t)$ and $p_2(t)$ present peaks, although the variations is very small. These peaks in the instantaneous populations account for the heat flux behavior, since this flux depends on the variation of the eigenpopulations.

As we are analysing the system's dynamics, positive flux means that the system is being pumped by some external energy transfer; while negative flux means that the system is giving energy to its environment.

As can be seen, in figure 5, the system is initially receiving heat from vacuum. As the system evolves in time it starts to lose heat and eventually come to a steady state, where the heat flux ceases, around the mark of 35 seconds.

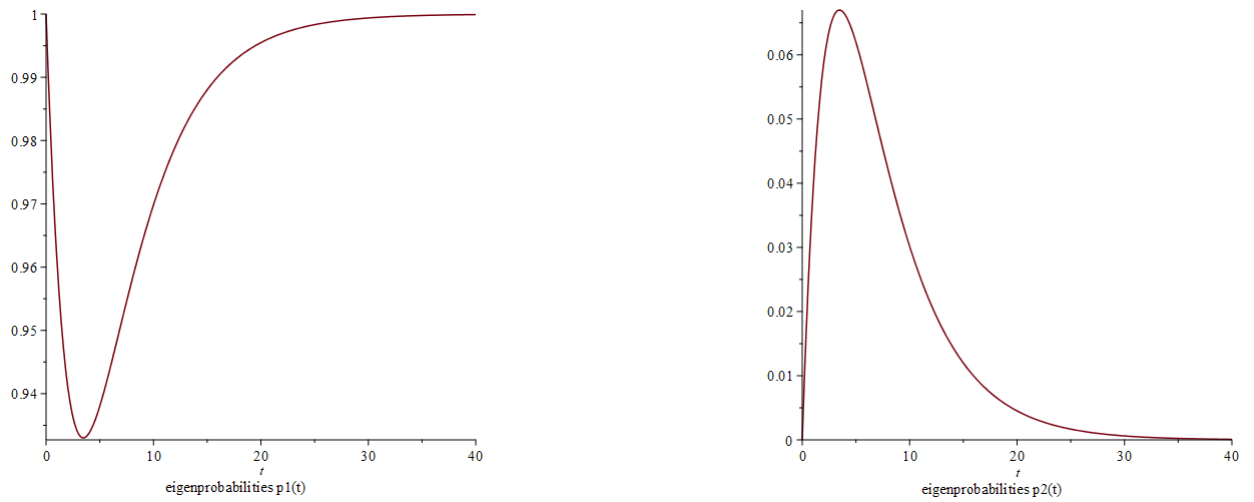


Figure 4 – Eigenprobabilities versus time.

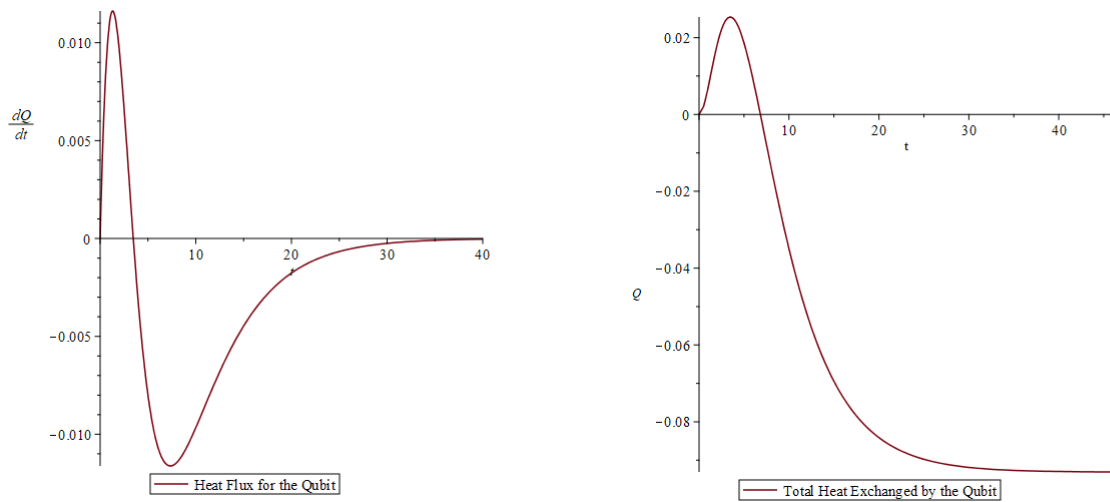


Figure 5 – In the first graph, on the left, we have the heat flux *versus* time for the qubit. As can be seen, the flux is initially positive, which means that the system is receiving energy in the form of heat from the environment. On the right we have the total heat exchanged, i.e. the integral of the heat flux.

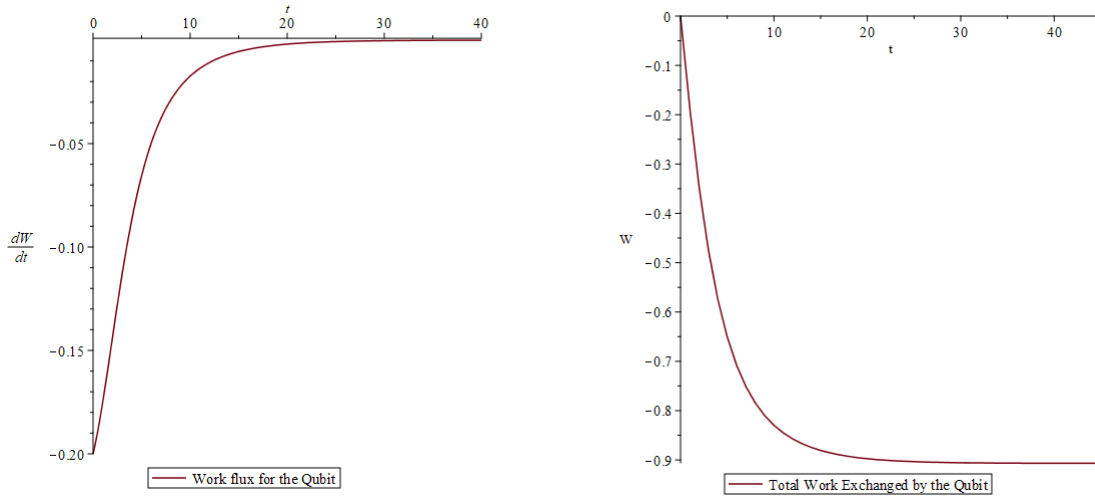


Figura 6 – Work flux from the qubit to the vacuum reservoir *versus* time; on the right, the total work exchanged.

The system also exchange energy in the form of work with the heat reservoir. This process occurs simultaneously with the heat exchange. The flux of work is negative, meaning that the system is losing energy to the bath. This behavior can be seen in figure 6. Note that in Alicki's formalism there is no work exchanged between the system and the reservoir. However, in the new definitions, the work is not null and comes from the initial coherence of the system.

To conclude this chapter, note that the general definition of heat is energy in transit. However, if we interpret the results presented in Fig. 5 as truly accounting for heat, as it was proposed by Ahmadi et al. and Alipour et al., we face a contradiction: the system is getting heat from the zero temperature bath. This possibly is indicating some inadequacy of the formalism.

5 Conclusions

The key idea of these new definitions for heat and work, from (18, 19) are based, according to the authors, on the Clausius reasoning, which defines heat as the portion of energy exchanged that accounts for entropy change and work as the energy exchanged that does not causes entropy change. With this in mind, the authors suggested that by differentiating the density operator in its spectral decomposition one should be able to acknowledge for two variations: one related to kets and bras evolution (unitary) and the other that is concerned with the variation of the instantaneous populations (non-unitary). With the aid of the von Neumann entropy, which varies as a function of the eigenvalues of ρ , the authors could identify the non-unitary part that arose from the tracking of the density operator, over time, as heat, while the part related to the kets and bras evolution were identified as work.

The fundamental difference between these new set of formulas for heat and work and the one used in Alicki's paper, is that the former splits the variation of the density operator into two parts, accounting for the so called "exchanged work". Therefore the new approach has one more term of work, which is not related to the contributions of external fields.

One of the main goals of these new proposals is to shed light into some inconsistencies that the standard formalism presents when applied to some cases, as in the example of the two qubits interacting. Although these formulas appeared, at first, to overcome the lack of consistency with the first law of thermodynamics, they failed when applied to a specific scenario, therefore suggesting that this new formalism is not general.

When we analysed the case of the two level atom interacting with the vacuum using the new definitions of heat and work, we obtained a very unusual behavior: the system absorbed energy from the vacuum reservoir. This fact seems to imply a possibly inadequacy of the formalism, since the vacuum reservoir should not be able to transfer energy to the system.

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